REMEDIATION OF OIL-BASED DRILL CUTTINGS USING LOW-TEMPERATURE THERMAL DESORPTION

by

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B.S., Wenzhou University, 2014

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
IN
NATURAL RESOURCES AND ENVIRONMENTAL STUDIES
(ENVIRONMENTAL SCIENCE)

UNIVERSITY OF NORTHERN BRITISH COLUMBIA

January 2017

Abstract

Drill cuttings are generated during the exploration and extraction of oil and natural gas. Due to the use of oil-based muds (OBMs) during drilling process, large amounts of oil-based drill cuttings (OBDCs) are produced. Such hazardous waste contains a relatively high content of petroleum hydrocarbons (PHCs). The effective removal of PHCs from OBDCs has attracted widespread attention since oil contaminants have severe impacts on the plant and animal ecosystem including human health (e.g., carcinogenesis and mutagenesis). Low-temperature thermal desorption (LTTD) treatment which both achieves relatively complete PHCs removal and keeps soil health at the maximum extent represent a feasible and promising method for the remediation of OBDCs. In this study, a bench-scale apparatus was used for the LTTD treatment of OBDCs with different PHCs contents. The effects of treatment temperature, treatment duration, sand/drill cuttings mixing ratio, and initial oil content on the removal efficiency of LTTD treatment for OBDCs were investigated. It was found that the PHCs was barely left in the high-oil-content drill cuttings (HOC) after LTTD (at 300 °C for 20 min), and thus its overall soil health was improved. LTTD of OBDCs was shown to follow nonlinear least-squares exponential kinetics (adjusted $R^2 > 0.9$), and the treatment under optimal operating conditions could both achieve Canadian management limits and minimum costs. Results are of practical guiding significance and may be used for designing effective LTTD treatment systems of OBDCs.

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Glossary

BFS	Blast-furnace slag
CAPP	Canadian Association of Petroleum Producers
CCME	Canadian Council of Ministers of the Environment
CMC	Critical micelle concentration
DCM	Dichloromethane
EA	Environmental Agency
EC	Electrical conductivity
EPA	Environmental Protection Agency
F2	Fraction 2
F3	Fraction 3
GC-FID	Gas chromatography - flame ionization detector
HOC	High-oil-content drill cuttings
HTTD	High-temperature thermal desorption
LOC	Low-oil-content drill cuttings
LTTD	Low-temperature thermal desorption
NFESC	Naval Facilities Engineering Service Center
NRC	National Research Council
OBDC	Oil-based drilling cuttings
OBM	Oil-based mud
PAHs	Polycyclic aromatic hydrocarbons
PC	Portland cement
PCBs	Polychlorinated biphenyls
PHCs	Petroleum hydrocarbons

RF	Response factor
S/C	Sand/OBDCs mass mixing ratio
S/S	Stabilization/solidification
SBDCs	Synthetic-based drill cuttings
SBMs	Synthetic-based muds
SD	Standard deviation
SFE	Supercritical fluid extraction
SWER	Solid Waste and Emergency Response
TC	Total carbon
TN	Total nitrogen
TPH	Total petroleum hydrocarbons
WBDCs	Water-based drill cuttings
WBMs	Water-based muds

Acknowledgement

This thesis reflects the final part of achievements that I have made in my M.Sc. study at the University of Northern British Columbia (UNBC). First and foremost, I would like to express my sincere gratitude to my co-supervisors, Prof. Jianbing Li and Prof. Min Zhao, for their patience, understanding, insightful instructions, and support throughout my study and research. Without their guidance and support, it would be impossible for me to complete this research. What I have learned from them will benefit my future career and life.

Moreover, I would like to thank Prof. Ronald W. Thring for serving as my supervisory committee member. I greatly appreciate his insightful comments, guidance and discussions. I would like to express my appreciation to Erwin Rehl and Charles Bradshaw working in Northern Analytical Laboratory Service (NALS) at UNBC for their patience and help on developing and refining my analytical methods as well as on analyzing my experimental samples. I also thank Conan Ma working at UNBC Chemstore for his support with sample delivery and lab materials supply.

Special thanks go to Prof. Joselito M. Arocena, a great soil scientist, who was my previous committee member. I am grateful to his kind guidance and help to my graduate study and life.

My gratitude also extends to the people in my lab group for their helps, valuable discussions and every joyful moment; they are Guangji Hu and Yuan Tian. Their kind sharing knowledge, skills and thoughts helped me a lot for the completion of this thesis.

Finally, I would like to dedicate this work to my family, my parents, grandma and my older sister, for their unconditional supports and understanding. Without their supports and encouragement, I would not have come to UNBC and complete my Master's degree.

Chapter 1 Introduction

Oil and gas industry generates a considerable amount of by-products and wastes which must be managed and treated properly (Qin et al., 2009). Oil-based drilling cuttings (OBDCs) are the major wastes generated during the process of oil/gas exploration and extraction (Talbi et al., 2009). Although part of oil-based muds (OBMs) are separated from drill cuttings and returned to the recirculation fluid system, they remain in the cuttings, which cause the formation of OBDCs (Khanpour et al., 2014). OBDCs from the solids control separation process usually contain 10-25% oil by weight (Childs et al., 2005; CAPP, 2000). Even after being treated with mechanical separation (e.g., drying shakers, drying centrifuges), OBDCs retain 5-10% oil by weight (Gerard and Antle, 2003; Reddy et al., 2003). As reported by Murray et al. (2009), the most common drilling muds used in British Columbia (BC) are OBMs, and thus large amounts of OBDCs containing relatively high content of petroleum hydrocarbons (PHCs) have been generated. According to Steven et al. (2014), BC government claimed to develop over 10,000 wells pumping shale gas to BC's coast to meet the vast liquefied natural gas exports to Asia. This would pose a great challenge for dealing with large amounts of drill cuttings, especially OBDCs, in BC.

The effective treatment of OBDCs has attracted widespread attention since oil contaminants have severe impacts on the plant and animal ecosystem including human health (e.g., carcinogenesis and mutagenesis) (Mandal et al., 2012). Traditionally, the on-site burial or landfill methods were selected to dispose of drill cuttings, but they are inadequate to meet current and future stringent environmental regulations due to their low efficiencies in removing contaminants (Ball et al., 2012). It is thus of great interest from industries and governments to find more cost-effective ways to remediate such waste materials. Many

remediation technologies for OBDCs have been proposed, including surfactant-enhanced washing (Yan et al, 2011), thermal (Stephenson et al, 2004) and microwave treatments (Robinson et al., 2010), supercritical fluid extraction (Goodarznia and Esmaeilzadeh, 2006), solidification and stabilization (Leonard and Stegemann, 2010), phytoremediation (Ji et al., 2004), and bioremediation (Alavi et al., 2014). Among these methods, thermal treatments by which soils are heated to remove volatile and semivolatile contaminants (e.g., mercury and hydrocarbons) from the media, are popular and versatile for their short treatment time and high removal efficiency (Aresta et al., 2008; Merino and Bucalá, 2007). According to the treatment temperatures, they are classified as low-temperature (100–350 °C) and high-temperature (350–600 °C) thermal desorption by physical separation, and incineration (600–1000 °C) which destroys contaminants (Falciglia et al., 2011). On one hand, limited reusability of residual soil after treatment and high initial setup expenses restrain the practicability of high-temperature thermal desorption (HTTD) (Yi et al., 2016). On the other hand, low-temperature thermal desorption (LTTD) treatment represents a feasible method for the remediation of oil contaminated soils which both achieves relatively complete remediation and keeps soil health at the maximum extent. According to Glenn et al. (2003), the first use of LTTD system to treat OBDCs from an offshore rig was at an onshore facility on the East Coast of Canada. This technology both achieved oil-on-cuttings discharge limitations and reduced costs through the recovery and reuse of base fluid. LTTD has been identified as a commercialized ex-situ technology for the remediation of PHCs-contaminated site such as drill wastes by National Research Council of Canada (NRC, 2008). It has been reported by industries and governments that many factors can affect LTTD treatment costs, including oil and moisture content of the waste, particle size distribution of the solids,

organic fractions and volatility, management of the waste. However, few researches have studied the in-depth effects of influential factors, desorption models of different PHCs fractions, as well as enhanced methods in the remediation of OBDCs using LTTD. Thus, a comprehensive study of the application of LTTD remediation to OBDCs is necessary (Onwukwe, 2014).

In this study, the LTTD treatment of OBDCs artificially spiked with different PHCs content was examined using a bench-scale apparatus. Ottawa sand was mixed with OBDCs with different mixing ratios to enhance the LTTD remediation process, as the additive could improve the texture and pore size of drill cuttings, thus increasing the effective diffusivity in porous media (Falciglia et al., 2011, Samaksaman et al., 2016a). The main objectives of the study were: (1) to analyze the changes of soil properties before and after thermal treatment, and examine the impacts of LTTD process on soil characteristics; (2) to develop and compare kinetic models for petroleum fractions and TPH desorption from OBDCs under different conditions by LTTD process; (3) to assess the influences of treatment temperature, sand/drill cuttings mixing ratio, and initial TPH content on the thermal desorption; (4) to evaluate the effects of treatment temperature, treatment duration, sand/ drill cuttings ratio, and initial TPH content on TPH removal efficiency; (5) to find optimal treatment conditions and to guide the design and the scale-up of LTTD system.

Chapter 2 Literature Review

2.1 Drill muds and cuttings

2.1.1 Characteristics of drill muds and cuttings

During the drilling process (Figure 2.1) for the exploration appraisal, and the production of oil and natural gas, drill muds (also known as drill fluids) are used to carry the rock phase up to the surface through the wellbore, lubricate the drill bit and control reservoir pressure (Hamed and Belhadri, 2009; Lee et al., 2011). The drill muds can be classified into water-based muds (WBMs), oil based muds (OBMs) and synthetic-based muds (SBMs) according to the base fluids used, which can be water, diesel/mineral oil, and non-aqueous fluids such as olefins, esters, and paraffin, respectively (McDonald and Portier, 2003; Breuer et al., 2004; Neff, 2005). OBMs and SBMs are used to drill a cleaner and more stable hole than WBMs, thus generating a lower volume of drill cuttings (Growcock et al., 2002). Consequently, OBMs and SBMs are generally preferred than WBMs in moist and deep conditions since they are capable of drilling a gauge hole and minimizing drilling problems (Ball et al., 2012). SBMs have lower toxicity, while diesel is usually used as a mud additive. Thus, the biodegradation properties of SBMs are similar to those of OBMs (Breuer et al, 2004). Although OBMs are more harmful to the environment due to the diesel/mineral oil content, they may still be the best option for some drilling conditions. Usually, OBMs contain about 30 to 90% diesel/mineral oil of the total volume of the mud (Kenny, 1993). OBMs are usually comprised of barite, clays, emulsifiers, water, chlorides, lignite, lime and heavy metals as additives (Neff, 2005; Ball et al., 2012; OGP, 2003), while about 10-50% of water containing chlorine salts (called saline brine) can be dispersed into the hydrocarbon phase to form a water-in-organic phase emulsion. Because of their toxicity, OBMs are

normally not discharged to the ocean but sent to the shore where they are reprocessed and reused (OGP, 2003).

Drill cuttings are mixtures of crushed rock chips, drill muds and some organic and inorganic chemicals (Rojas-Avelizapa et al, 2005). For example, Table 2.1 summarizes the characteristics of drill cuttings in the North Sea and Red Sea. The particle size of drill cuttings ranges from ~ 2 μm (clay) to > 30 mm (coarse gravel). Due to different geochemistry of the formations being drilled and the amount of drill muds adhering to the cuttings, drill cuttings usually contain different quantities of petroleum hydrocarbons (PHCs) mostly with carbon number of C_{10}–C_{28}, inorganic salts and heavy metals (e.g., barium, chromium, cadmium, zinc, and lead) which are from mud additives and naturally existing minerals in the formations (Onwukwe and Nwakaudu, 2012; Neff, 2005; Goodarznia and Esmaeilzadeh, 2006). Most of the metals from geologic formations associated with cuttings are in immobile forms and not bioavailable (Neff, 2005). Drill cuttings are categorized as water-based drill cuttings (WBDCs), oil-based drill cuttings (OBDCs) and synthetic-based drill cuttings (SBDCs) based on the use of WBMs, OBMs and SBMs, respectively. WBDCs may contain small quantities of PHCs which may be from the additives (e.g., lubricants) of the mud, or from the geologic strata being drilled (Neff, 2005). This kind of drill cuttings are considered to pose little or no risk to the environment. US EPA allows the discharge of such cuttings to federal waters (> 3 miles from the shore) if they meet restrictions stipulated in the Effluent Limitation Guidelines (OSPAR Commission, 2013). However, WBDCs are forbidden to discharge if they are with PHCs. They also need pretreatment to reduce the high liquid content and salinity before they are disposed of using landfill. In the Gulf of Mexico, only SBDCs containing less than 6.9% (by mass) olefin or 9.4% (by mass) ester can be

discharged to Federal waters. OBDCs usually containing high content of PHCs are prohibited to discharge to State or Federal Waters in the US (Ball et al., 2012). In Europe, untreated OBDCs and SBDCs are assigned to the *Controlled Management of Hazardous Waste 2000* (EC) (OSPAR Commission, 2001), and oily drill cuttings generated offshore must be cleaned to have less than 1 wt% residual oil (Muherei and Junin, 2007).

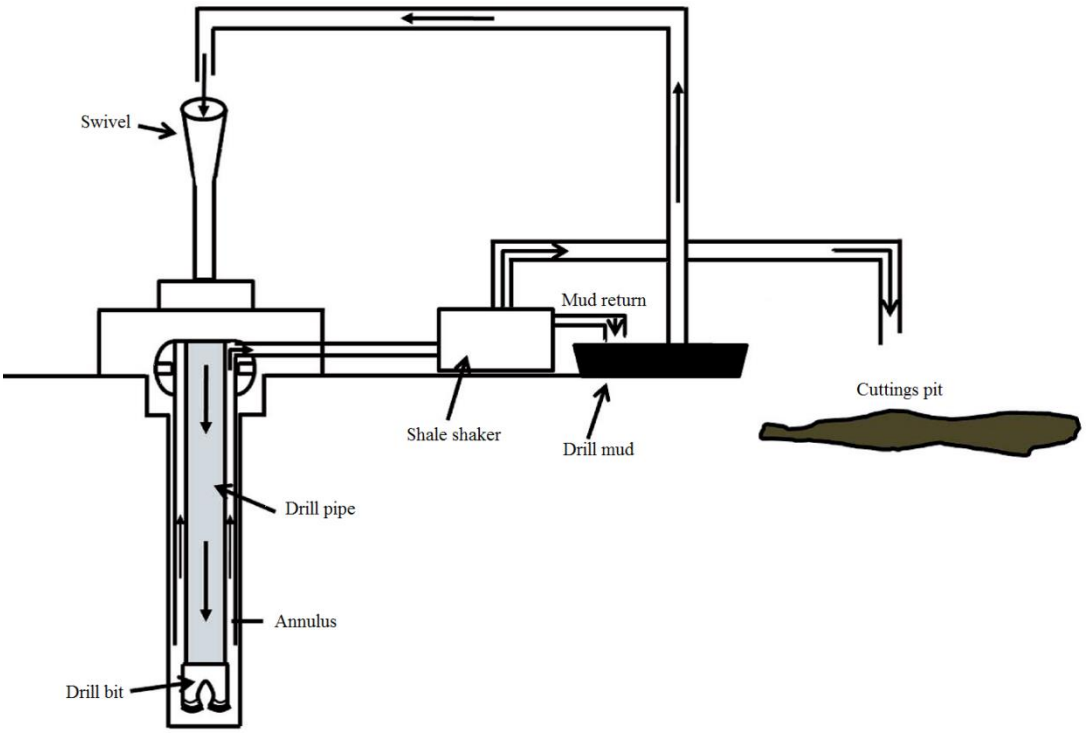


Figure 2.1 Schematic illustration of the drilling process (Ball et al., 2012)

Table 2.1 Properties of drill cuttings in the North Sea and Red Sea (Al-Ansary and Al-Tabbaa, 2007)

Property	North Sea drill cuttings	Contaminant	North Sea drill cuttings		Red Sea drill cuttings	
			Ave., wt%	Max., wt%	Ave., wt%	Max., wt%
Sand content	8–33%	Hydrocarbons	4.20	22.40	10.95	11.80
Silt content	37–62%	Barium	4.90	29.80	0.20	1.20
Clay content	16–25%	Chromium	0.005	0.02	0.10	0.40
Water content	14–35%	Lead	0.02	0.10	0.10	0.25
pH	8–10.1	Zinc	0.03	0.10	0.10	0.40
		Chlorides	2.03	2.26	2.13	9.20

2.1.2 Toxicity and impact of OBDCs

The main contaminants in OBDCs are PHCs, which consist of alkanes, cycloalkanes, benzene, toluene, xylenes, phenols, and various polycyclic aromatic hydrocarbons (PAHs) (Hu et al., 2013). These substances are considered hazardous pollutants, and some compounds are recalcitrant in the environment and can bio-accumulate in food chains, thus threatening human health (e.g., carcinogenesis and mutagenesis) (Hentati et al., 2013; Mandal et al., 2012).

After being introduced into the terrestrial environment, PHCs in OBDCs can shift the physical and chemical properties of target soils, resulting in soil morphological change (Robertson et al., 2007). Due to the hydrophobicity of PHCs, they would cause decreased hygroscopic moisture, hydraulic conductivity, and water retention capacity of soils, and thus

restrain soil water/air exchange (Tang et al., 2012). The oil brought in soil from OBDCs may also inhibit the availability of nutrients, hamper seed germination, and restrict plants growth (Al-Mutairi et al., 2008). All of these can have negative effects on agricultural production (Wang et al., 2008). The PHCs in soils could also migrate down through the soil profile and enter the local groundwater, leading to unsafe drinking water and even triggering ecological disasters (Wang et al., 2008). Moreover, PHCs could inhibit the activity of soil enzymes (e.g., hydrogenase and invertase) and microorganisms (Suleimanov et al., 2005).

2.2 Remediation technologies for OBDCs

2.2.1 Surfactant-enhanced washing

Surfactants are surface active compounds which are amphiphilic due to the unique structure with hydrophilic head and hydrophobic tail (Mulligan, 2009). Surfactants with oil-like and water-like portions can accumulate at the interfaces of both oil and water, thus reducing the interfacial tension of oil/water system and mobilizing the hydrocarbons from the soil surface by reducing the capillary force holding oil and soil together (Pacwa-Płociniczak et al., 2011). When aqueous surfactant concentration exceeds the critical micelle concentration (CMC), surfactants associate to form micelles, which dramatically increase the solubility of oil. It has been proved that water-based washing remediation is highly inefficient when capillary-bound oil exists in the porous medium. However, by reducing the interfacial tension and forming micelles, surfactants can be used to enhance the solubility and mobility of hydrocarbons for soil washing or flushing systems.

According to Sabatini et al. (2001), field demonstrations indicated that traditional subsurface remediation by water-based washing treatment was highly inefficient, while

surfactant-enhanced washing remediation can efficiently and economically remediate OBDCs. It was found that 4 wt% of anionic surfactant can remove 99% (by weight) oil from drill cuttings with 10 - 20% oil content via solubilization effect. The washing results showed that after treating with low surfactant concentration of 0.1 wt%, drill cuttings' final oil concentrations were reduced to 4 - 5 wt%, with 70 to 85% removal efficiencies. In an Environmental Protection Agency (EPA) project, surfactant (Alfoterra 145-4PO), a branched alcohol propoxylate sulfate with a high content of mono-branched isomers, was used to remove oils from OBDCs (Sabatini et al., 2002). In this project, to reduce soluble Ca^{2+} in drill cuttings which can precipitate surfactant, Na_2SiO_3 was added to promote Ca^{2+} precipitation, and the octyl-sulfobetaine was used to relieve the high hardness and high hydrophobicity of OBDCs. As a result, surfactant loss was minimized and hydrocarbons removal efficiency was maximized. For instance, more than 85% of the surfactant remained in the system after washing, and the oil content of OBDCs after 30 min washing treatment was reduced from 20 wt % to 2 – 5 wt %. The process conditions with 20 wt % of oil being reduced to 3 wt % were proposed for a future pilot-scale test: 13% Na_2SiO_3, 0.1% Alfoterra 145-4PO and 1% octyl-sulfobetaine.

Biosurfactants are mainly produced by bacteria and fungi. According to the chemical structures, they are generally classified into five groups: glycolipids (e.g., rhamnolipids, trehalolipids, sophorolipids), lipopeptides (e.g., surfactin, lichenysin), phospholipids (e.g., phosphatedylethanolamine), fatty acids (e.g., corynomycolic acid, spiculisporic acid), polymeric biosurfactants (e.g., emulsan, alasan, biodispersan, liposan, mannoprotein) (Pacwa-Płociniczak et al., 2011). Compared to chemical surfactants, biosurfactants are environmentally friendly, biodegradable and less toxic, which can increase their

environmental benefits of application (Muherei and Junin, 2007). Yan et al. (2011) investigated the effect of five influencing factors (biosurfactant concentration, liquid/solid ratio, washing time, stirring speed, and temperature) on the rhamnolipid-enhanced washing remediation of OBDCs. It was found that the TPH of the drill cuttings dropped from 85,000 to 12,600 mg/kg under the optimal conditions (rhamnolipid concentration, 360 mg/L; liquid/solid ratio, 3:1; washing time, 20 min; stirring speed, 200 rpm; temperature, 60 °C), and the TPH removal increased with the rise of values of the five studying parameters within a certain range.

Although surfactant-enhanced washing is effective and promising in remediating OBDCs, there are some limitations when applying to large-scale field work, including effectiveness, full-scale cost, public and regulatory acceptance, biodegradability, toxicity, and ability to recycle (Strbak, 2000). Particularly, the costs of biosurfactants production may restrict their commercial applications, but the related costs can be decreased by improving yields, recovery, and using low-cost or waste substrates (Calvo et al., 2009). More researches about the remediation of OBDCs using various biosurfactants should be studied. In addition, this technology is hard to reduce oil content to be less than 1 wt% in the drill cuttings, which means post treatment such as biodegradation should be conducted before direct discharge (Yan et al., 2011).

2.2.2 Stabilization and solidification

Stabilization/solidification (S/S) is a widely-used technology in waste management (Sobiecka et al., 2014). S/S uses stabilized/solidified products to immobilize contaminants (e.g., heavy metals and PHCs) in drill cuttings, thus reducing their hazardous nature or enabling their reuse as construction products (Al-Ansary and Al-Tabbaa, 2007; Leonard and

Stegemann, 2010a). Stabilization converts the contaminants into less soluble or toxic forms, and the main effect for immobilization of PHCs in drill cuttings is sorption onto the surface of hydraulic binders (Ball et al., 2012). Solidification engages encapsulation of contaminants by creating a durable solid matrix (Kameswari et al., 2014). Cement based processes or a combination of cement and pozzolans (e.g., fly ash, lime, volcanic ash) are mainly used in the S/S applications (Xin et al., 2016). Leaching tests for S/S products are usually used to determine the effectiveness of the treatment (Wang et al., 2014). Al-Ansary and Al-Tabbaa (2010) investigated the performance of conventional S/S binders including Portland cement (PC), lime and blast-furnace slag (BFS), and novel binders (i.e. microsilica and magnesium oxide cement) for synthetic petroleum drill cuttings. The leachability results showed that oil stabilization increased with the increase in the percentage of binder added, and the 20% BFS–PC and 30% lime–PC binders converted the drill cuttings with low oil content (4.20 wt%) to a stable non-reactive hazardous waste satisfying the UK landfill acceptance criteria. By using factorial design method, Leonard and Stegemann (2010b) found that waste/binder ratio, high carbon fly ash addition, and curing time had significant impacts on the performance of S/S products. The leaching of hydrocarbons was dramatically decreased with the addition of high carbon fly ash since it increased the surface area for sorption.

S/S can be applied quickly with low cost since it requires low energy in industry and the cement and some industrial by-product binders (e.g., pulverized fuel ash or ground granulated blast furnace slag) with low price are used as stabilized/solidified material (EA, 2004; Paria et al., 2006). In addition, the potential of reusing S/S products as a construction material increases the economic benefit of S/S technique. Laboratory tests are necessary to be conducted to determine the proper binders to achieve the desired requirements prior to large-

scale application (Ball et al., 2012). S/S has been widely applied to the treatment of inorganic waste due to its effectiveness. However, its application to oil contaminated drill cuttings still needs to be investigated and improved since organic compounds (i.e. hydrocarbons) have detrimental effects on the hydration of binders (Conner and Hoeffner, 1998; Qian et al., 2006). With little chemical uptake of organics into hydration products, non-polar hydrocarbons are more likely to be retained by physical entrapment and sorption, while polar compounds will remain leachable (Karamalidis et al., 2007; Leonard and Stegemann, 2010a). This will cause long-term environmental risks. Therefore, large-scale and long-term S/S processes should be further studied, and the improvement of hydrocarbons immobilization using additives can be explored. The combination of S/S with other technology such as bioaugmentation may be a new research direction since the amended microorganisms eventually breakdown the organic contaminants (Kogbara et al., 2016).

2.2.3 Supercritical fluid extraction

Supercritical fluid extraction (SFE) is one of the most widely used and studied new technologies for the removal of contaminants from the polluted substances (Sharif et al., 2014). It is attractive since the supercritical fluids allow the product to be free from residual solvent while the fluids can be completely removed from the polluted matrixes (Pourmortazavi and Hajimirsadeghi, 2007; Esmaeilzadeh and Goodarznia, 2005). The supercritical fluids can be obtained under pressure and temperature that are above the critical point of certain compound, mixture or element (Sharif et al., 2014). Carbon dioxide (CO_2) is commonly used at supercritical conditions as a solvent in the SFE process due to its environmentally-friendly, inert, cheap, widely-available, nonflammable and nonexplosive characteristics (Khanpour et al., 2014; Goodarznia and Esmaeilzadeh, 2006). Supercritical

CO_2 with excellent solvating features are easily used to dissolve nonpolar compounds (e.g., diesel and mineral oils) (Khanpour et al., 2014). The SFE technique has been applied for the removal of contaminants from the dense matrixes in many studies. Rajaei et al. (2013) found that supercritical CO_2 was successful to remove pollutants from contaminated R-134 catalyst and Tonsil CO 610 G clay soil. Chen et al. (1997) reported that after 30 min of extraction with SFE unit at 313 K and 100 bar, over 86% of polychlorinated biphenyl (PCB) in Hudson River sediment and approximately 92% in St. Lawrence River sediment were removed. The results exhibited that SFE is an effective and promising technology for cleaning up PCB contaminated soil/sediment.

Based on the knowledge of SFE technique, a few investigations were reported on the removal of contaminants from OBDCs to find the potential of using supercritical CO_2 extraction process in OBDCs remediation. Goodarznia and Esmaeilzadeh (2006) used supercritical CO_2 to extract oil from OBDCs over a temperature range of 55 to 79.5 °C, and at a range of pressures (160 to 220 bar). Based on drill cuttings weight loss, results showed that a minimal extraction efficiency of 22.4% in one step extraction was obtained at 180 bar and 60 °C, while 49.1% of oil was extracted at 200 bar and 79.5 °C. It was also found that the extraction efficiency increased with temperature. Esmaeilzadeh et al. (2008) investigated the solubility of oil-contaminated drill cuttings in supercritical CO_2 process by using the PC-SAFT EOS model. The results showed that the solubility of TPH (C_{10}, C_{11-}, C_{12+}) was reduced by decreasing the temperature, and the model had good performance in predicting the solubility of a heavy hydrocarbon mixture in OBDCs by supercritical CO_2 extraction. Khanpour et al. (2014) investigated the effects of different factors including extraction temperature, pressure, flow rate of CO_2 and static time on the removal of contaminations

from drilling mud. It was found that the maximum amount of extracted contaminants (0.7702 g/L) occurred at operational conditions with flow rate of 0.5 cm^3/s, static time of 120 min, pressure of 100 bar, and temperature of 313 K. The results also showed that with the flow rate increasing from 0.05 to 0.1 cm^3/s, the content of extracted contaminants remained steady, while a significant reduction of extracted contaminants appeared with the further flow rate increasing from 0.1 cm^3/s to 0.14 cm^3/s, and then the extracted amount kept constant at flow rate from 0.14 cm^3/s to 0.36 cm^3/s. The removal efficiency of contaminants had a positive correlation with temperature in the range of 313–338 K. In the extraction pressure range of 100 to 180 bar, the removal of contaminants increased with the growth of pressure, while further pressure increasing up to 200 bar led to no significant effect. Similarly, between the static time of 20-110 min, raising time led to higher extraction efficiency, while further static time increase had no significant effect on the removal efficiency. In addition, X-ray powder diffraction and scanning electron microscopec tests illustrated that the supercritical CO_2 extraction was capable of removing pollutants from the contaminated drilling mud. As a result, the SFE technology can be considered as an applicable and appropriate method to remove contaminants from OBDCs.

However, the high cost restrains the industrial application of SFE for contaminant removal. Previous research studies did not show a high oil removal from OBDCs or did not present detailed removal efficiency of hydrocarbons. The effectiveness and costs of large-scale SFE process should also be studied. In addition, the optimization of extraction conditions for the SFE technique is necessary before field applications. Experimental design is very useful for conducting SFE process to find optimal conditions since designed

experiments can give systematic investigation, screening and summarizing the SFE affecting factors (Sharif et al., 2014).

2.2.4 Bioremediation

Bioremediation is defined as the process of using biological agents (mainly microorganisms and their enzymes) to restore the polluted sites by removing hazardous contaminants, and is generally utilized for the remediation of oil-contaminated environments via accelerating the biodegradation of PHCs into non-toxic and simpler inorganic compounds, mostly CO_2 and water (Lin et al., 2010). Due to its simplicity and low costs, bioremediation has been proved to be a promising method of removing oil from OBDCs (Alavi et al., 2014). As a biological process, the rate of bioremediation depends on the environmental conditions (e.g., nutrients, temperature, pH, available oxygen, salinity, texture and moisture of the OBDCs), the fractions and content of PHCs to be degraded and the type of treatment utilized (e.g., composting, bioreactor, and land farming/spreading) (Tyagi et al., 2011; Ball et al., 2012).

For accelerating the bioremediation of OBDCs, biostimulation and bioaugmentation are usually used to improve the slow natural biodegradation of PHCs. The approach of biostimulation focuses on the identification and adjustment of factors such as nutrients to improve the population and activity of indigenous microbes capable of degrading PHCs, thus facilitating the biodegradation (Couto et al., 2010). Bioaugmentation introduces PHCs degrading microorganisms (usually single strains or consortia), which are highly concentrated and specialized, to an oil-contaminated system (Couto et al., 2010). Okparanma et al. (2009) isolated two bacteria (*Bacillus subtilis* and *Pseudomonas aeruginosa*) and investigated their effectiveness of remediating oily drill cuttings contaminated with PAHs.

Laboratory tests showed that after 6-week treatment, *Pseudomonas* was with better ability of degrading the 3- and 4-ring PAHs, and both bacterial strains well degraded the 5- and 6-ring PAHs. However, limited degradation of the 5-ring PAHs appeared by using the mixed culture of bacterial isolates. The first-order degradation rate of persistent PAHs by isolated bacteria varied from 1.9×10^{-4} to 9.3×10^{-2} d^{-1}. Steliga and Jakubowicz (2010) compared the efficiency of basic bioremediation and inoculation with biopreparations based on indigenous bacteria and fungi on drilling waste remediation. It was found that after 135 days of treatment, basic bioremediation stimulated under optimum conditions to facilitate the growth of native microorganisms, degraded 52.3–72.5% of TPH, whereas bioaugmentation with prepared inoculation reached a TPH reduction of 93.8–94.3%. Results showed that the first-order biodegradation rate constants for bioaugmentation (0.0150–0.0181 d^{-1}) were much higher than those for basic bioremediation (0.0055–0.0068 d^{-1}). It was also demonstrated that bioaugmentation had significant improvement ability due to a relatively high degree of biodegradation for n-C23–n-C36 hydrocarbons and should be used to assist basic bioremediation. Fan et al. (2012) used both biostimulation amended with inorganic nutrients (C:N:P ratio of 100:10:1) and bioaugmentation inoculated with a well-adapted bacterial consortium to remediate waste drilling fluid with initial TPH of 15,300 mg/kg in bioreactors. It was found that after 120 h, the total removal efficiency of TPH in the abiotic control was 15.7%, while the TPH removal for fluid without inoculation (biostimulation) and with inoculation (bioaugmentation) were 58.3% and 91.2%, respectively. These results indicated that bioaugmentation with selected microbial strains could produce more effective bioremediation treatment. Alavi et al. (2014) studied the effects of nutrients on PHCs biodegradation in OBDCs through a slurry bioreactor. During 21 days of remediation, the

TPH removal efficiency under the C/N/P ratio of 100/5/1 and 100/10/2 were 90.5 % and 92.5 %, respectively, indicating that increasing the amount of nitrogen and phosphorous couldn't enhance microbial biomass and TPH removal efficiency.

The limited availability of hydrocarbons to microorganisms restricts the efficiency of bioremediation. Therefore, biosurfactants which can reduce the interfacial tension, thus improving the bioavailability of oil, have recently received much research attention for enhancing biodegradation (Szulc et al., 2014). For example, the improved TPH removal was observed in a study by Yan et al. (2011) that used a rhamnolipid solution to wash OBDCs, followced by bioremediation with a mixed bacterial culture. After 120 days of biodegradation, the TPH in drill cuttings decreased from 16,900 ± 530 mg/kg to 5470 ± 370 mg/kg, corresponding to a removal efficiency of 67.3%.

There are few field-scale applications of the bioremediation treatment for OBDCs, since bioremediation is subjected to a variety of factors such as natural environmental conditions, PHCs content, activities of microorganisms and bioavailability of the contaminants (Van Hamme et al., 2003). These factors are hard to control in the field. Extreme conditions such as cold weather and flood may also cause the failure of bioremediation (Yang et al., 2009). The contaminated site remains long-term toxicity since bioremediation cannot reduce the contaminant oil level in a short time and heavy oil residues may be left behind in the waste, resulting in incomplete remediation (Płaza et al., 2005; Agarwal and Liu, 2015).

2.2.5 Phytoremediation

Phytoremediation is the use of green plants and their associated microorganisms to stabilize or reduce toxic metals, organics and radioactive substances in contaminated soil,

sediment, surface and groundwater (Macek et al., 2008; Soleimani et al., 2010; Zhou et al., 2011). Plant roots can incubate a favorable environment for the degradation of organic contaminants in soil matrix (Soleimani et al., 2010). Plant root system promotes the water and gases movement through the soil due to the improvement of soil structure. The active rhizosphere also fosters microbial activity and increases the bioavailability of pollutants. The aboveground plant tissues with contaminants are finally harvested for safe disposal. Thus, the plant-based technology is a promising green process for the remediation of PHCs contaminated wastes and has been applied to oil contaminated soil by many researchers (Zhou et al., 2011).

Some researchers also investigated the use of phytoremediation in OBDCs remediation. Ji et al. (2004) carried out a 2-year in situ pilot experiment using the mature reed wetland to remove hydrocarbons from polluted drill cuttings with 3 wt% of extra heavy oils. One control bed and three reed treatment beds were used to treat soil mixed with various amount of drill cuttings: 0 (control), 5 (reed bed #1), 20 (reed bed #2), and 40 (reed bed #3) kg/m^2 and. Results indicated that although without additional fertilization, the mature reed wetland was effective for degrading extra heavy oils, and the oil removal efficiency increased with treatment time. The majority of extra heavy oils was degraded in the first year, and around 0.1, 10 and 40 mg/kg of extra heavy oils were left in reed bed # 1-3, respectively, after 2-year treatment in the surface soil layer. The reed yield was significantly inhibited in reed bed # 3 with the highest extra heavy oils content in the first year, whereas reed yield recovered vigorously during the long-term treatment. Choi and Chang (2009) conducted a pot experiment planted with white spruce (*Picea glauca [Moench] Voss*) seedlings to remove residual hydrocarbons from composted drilling wastes with different composting ages (1, 2,

3, and 4 years, coded as 1Y, 2Y, 3Y, and 4Y, respectively). The highest TPH removal was observed in the 3Y compost (41.1%), while the lowest was in the 1Y compost (9.3%). The N fertilization improved the TPH degradation in the 1Y (from 9.3 to 15.3%) and 4Y composts (from 14.3 to 22.6%) which were with low initial NH^{4+} contents.

Studies showed that phytoremediation can be a promising and environmentally friendly alternative for the treatment of OBDCs. However, there is still a long way to properly apply phytoremediation to the field-scale treatment. A 3-year field phytoremediation conducted in Milwaukee, USA, using plants (i.e. black willow, prairie cord grass, lake sedge, annual rye, and bulrush) did not improve PAHs removal relative to non-plant treatment (Smith et al. 2008). This may be due to the nutrients competition between plants and soil microorganisms, thus inhibiting the microbial degradation of PAHs in the rhizosphere. Uncontrollable environmental parameters such as precipitation, temperature, nutrients and pathogens in the field may affect seed germination and plant growth, which can have negative effects on phytoremediation (Zhou et al., 2011). In addition, it is probable that accumulated contaminants in plants are conversely released into the environment in field applications. Considering potential difficulties of field scale phytoremediation, further management practice needs to be explored. More effective and resistant plants and soil amendments can be explored to enhance phytoremediation efficiency.

2.2.6 Microwave heating

Microwave heating directly transports energy to substances, resulting in all single elements of the material being heated instantly via agitation of polar molecules or ions under the effect of an oscillating electric or magnetic field (Shang et al., 2006; Mutyala et al., 2010). Based on the response to microwaves for diverse materials, the interactions between

material and microwaves are classified into three categories: transparent (low dielectric loss materials e.g., sulfur take in little microwaves), opaque (conductors e.g., copper reflect microwaves) and absorbing (high dielectric loss materials e.g., water absorb microwaves) (Robinson et al., 2010; Mutyala et al., 2010). Therefore, microwave heating is not applicable to all materials. Microwave treatment has apparent benefits in dealing with materials consisting of absorbers and transparent components. The elements with a high dielectric loss absorb much more microwave energy than the transparent substances, resulting in selective heating and causing the removal of targeting contaminants (Shang et al., 2006). Microwaves, with rapid heating, penetration, and selectivity, have been an attractive alternative technology in the fields of hydrocarbons separation from oil contaminated wastes (Mutyala et al., 2010). Many studies have been reported in the application of microwave treatment to the remediation of OBDCs. Shang et al. (2006) examined the effects of power, treatment time and moisture content on the oil removal from OBDCs by microwave heating. The lab tests illustrated that the oil removal efficiency could be increased by increasing the cavity power, residence time and moisture content, and under certain conditions the residual oil can be reduced from 16% to below 1%. Robinson et al. (2008a) used microwave to assist nitrogen and steam stripping processes for OBDCs, which greatly enhanced the oil desorption rate. It was demonstrated that the addition of microwave-absorbing materials such as carbon-rich additives or recycled char could induce pyrolysis during the microwave treatment, while pyrolysis also occurred in drill cuttings which contained just water as the microwave-absorbing phase (Robinson et al., 2008b). By using high microwave power, water alone can act as a microwave receptor to induce pyrolysis of hydrocarbons, leading to a high temperature of over 300 °C in the drill cuttings, which can drastically improve the oil

removal efficiency. A pilot-scale continuous microwave treatment process for the remediation of OBDCs was developed by Robinson et al. (2009). It was found that the residual oil levels could be reduced to below 1%, satisfying the current offshore discharge limit, and even to 0.1% that is within the classification for non-hazardous waste. The continuous system was able to consume lower energy but obtain higher oil removal than equivalent batch processes. Robinson et al. (2010) also proved that the continuous microwave system with bulk materials handling capacity was robust by using electromagnetic design and process engineering concepts. Petri et al. (2015) indicated that the increase of initial drilling fluid content in drill cuttings reduced the oil removal efficiency during the microwave remediation, but the mechanical agitation of the microwave bed improved the removal efficiency by up to 17%, while the type of drilling fluids in drill cuttings did not significantly influence the removal kinetics.

Microwaves treatment has been illustrated to be a quick and effective technology in the remediation of OBDCs by many researchers. However, few studies were reported to apply this technology commercially due to the high initial setup costs and its uncertain potential. If microwave remediation is demonstrated to be with high remediation efficiency and profits on a large scale, it could have a considerable impact on petroleum industry (Mutyala et al., 2010).

2.2.7 Thermal treatment

Thermal treatment is a remediation technique by which soils are heated to remove volatile and semivolatile contaminants (e.g., mercury and hydrocarbons) from the media (Chang and Yen, 2006; Aresta et al., 2008). According to thermal treatment temperatures, it can be classified as low-temperature (100–350 °C) and high-temperature (350–600 °C)

thermal desorption as well as incineration (600–1000 °C). Thermal desorption has been used to remove hydrocarbon contaminants from solid wastes including OBDCs with high efficiency (Zupan and Kapila, 2000; Stephenson et al., 2004; Onwukwe, 2014). The cuttings must first be pre-dried to vaporize water and reduce energy costs, since water evaporates first during the treatment. Oil with a higher boiling point evaporates after the water.

Pi˜na et al. (2002) studied the impact of soil composition and final temperature (200–900 °C) on the weight loss of diesel-contaminated soil (with 2.5 wt% of diesel). Researchers have found that final temperature, treatment time and soil properties (e.g., soil texture) are the key factors of thermal remediation efficiencies (Falciglia et al., 2011). Samaksaman et al. (2015) conducted a laboratory-scale thermal treatment of lube oil contaminated soil under 800 °C using fixed/fluidized bed and found that the addition of sand to polluted soil could enhance oil removal. Samaksaman et al. (2016b) also demonstrated that a two-stage fluidized bed thermal treatment under 500-700 °C and 40 min treatment duration could remove 98.27 % to 99.93 % of initial oil from polluted soil. Onwukwe (2014) applied thermal desorption to OBDCs containing 21.8% of oil at 800 °F (427 °C) for 45 min, with only 0.33% of oil left in the drill cuttings, suggesting that thermal desorption treatment can relatively completely remove oil from OBDCs.

However, limited reusability of residual soil and high initial setup cost restrain the practicability of high-temperature thermal desorption (HTTD) (Yi et al., 2016). Low-temperature thermal desorption (LTTD) becomes more attractive in oil-contaminated wastes remediation. It has been demonstrated that LTTD is sufficient to treat OBDCs, wastes with light oils (Kapila and Thomas, 2003; Seaton et al., 2006). Besides, less inherent thermal degradation of the base oil in OBDCs under LTTD treatment, and thus recovered oil can be

reused in the mud system (Fang et al., 2007). Falciglia et al. (2011) investigated the effects of soil texture and treatment time on the oil removal from diesel contaminated soils under LTTD (100–300 °C). Results showed that within 30 min of thermal desorption, a temperature of 175 °C was capable of cleaning up diesel polluted sandy and silty soils to below 0.1% of oil content, while a higher temperature (250 °C) was required for clay soils. To understand the reusability of LTTD remediated soil in agricultural systems, O'Brien et al. (2016) treated uncontaminated topsoil and subsoil at 350 °C. Results showed that organic carbon in both thermal treated topsoil and subsoil decreased over 25%, and the total aggregation was reduced by 20% in the topsoil while there was no change in the subsoil. This study indicated that thermally treated soils could still be reused for plant cultivation although the soil properties were changed compared with untreated soil, but the treated soil may require additional management such as soil amendments. Yi et al. (2016) investigated the LTTD treatment (at 200 °C for 15 min) of oil-contaminated soil with 5133±508 mg/kg of TPH, and evaluated the change of soil ecological and physicochemical properties after LTTD treatment. It was shown that the general soil health associated with biological yield and environmental functions was enhanced after LTTD, indicating that LTTD could be a better alternate method compared to other harsh remediation processes. However, to achieve better soil quality, ecological functions of thermally treated soil should be improved.

LTTD treatment has been proved to be a more feasible method in thermal treatment which both achieves relatively complete remediation and keeps soil health at the maximum extent. It has also been regarded as an innovative technique by Environment Canada (2013), as it is cost effective and environmentally friendly alternative. In addition, the solid treated by LTTD could be returned to the initial excavation site as clean backfill. According to

National Research Council of Canada (NRC, 2008), LTTD has been recognized as a commercialized ex-situ technology for the remediation of PHCs-contaminated soil such as drilling wastes. However, more researches should be studied in the OBDCs remediation using LTTD. The effects of factors such as final temperature, treatment time, and initial oil content on the TPH removal of OBDCs by LTTD should be investigated in depth. Moreover, enhanced methods should be investigated. For example, the addition of sand to soil could enhance the effective diffusivity of hydrocarbons in soil (Falciglia et al., 2011) and improve the thermal conductivity of soil (Samaksaman et al., 2016a). Kinetics for different oil fractions removal and energy consumption of LTTD should also be examined to better understand the application OBDCs remediation. Furthermore, large-scale experiments are required before field application.

2.3 Summary

OBDCs generated during the drilling process for the exploration appraisal, and the production of oil and natural gas have been a worldwide concern. Such wastes require effective treatment due to the high risks they may pose to the environment and human health. Traditional on-site burial or landfill methods are not environmentally benign means for clean-up, and the microbial degradation of oil contaminants can be very time-consuming. Some recently developed treatments such as microwave heating, HTTD and incineration may be very promising in terms of oil recovery and/or the decontamination of OBDCs, but their capital and/or operating costs could be very high, or their implementation to large-scale treatment might be infeasible. The effectiveness, reuse and recovery of surfactants, and full-scale cost have to be considered when applying surfactant-enhanced soil washing at large scale. Only using SFE treatment may not satisfy the reuse and disposal requirements for

OBDCs and its efficiency should be improved before application. For bioremediation and phytoremediation, the contaminated soil remains long-term toxicity since both of them cannot reduce the contaminant oil level in a short time, while the heavy oil residues may be left behind in the waste, causing incomplete remediation. Thermal treatments have been studied and used effectively in remediating oil contaminated soil. However, there are few researches done in the remediation of OBDCs using thermal treatments. LTTD treatment which both achieves relatively complete remediation and keeps soil health at the maximum extent represent a feasible method for the remediation of OBDCs, and is thus examined in this thesis study.

Chapter 3 Methods and Materials

3.1 Base soil samples

Uncontaminated forest and sandy soils were collected from the forest (53°52'15.1"N 122°47'28.4"W) near UNBC and the riverside (53°56'07.4"N; 122°47'41.5"W) of Nechako River in Prince George, BC, Canada, respectively. The soil samples were oven dried under 60 ºC for 2-4 days and screened through a No. 20 mesh sieve to remove rocks, roots and leaves, and were subsequently stored in the fridge at 4 ºC. The two soil samples were mixed and used as base soil for synthetizing OBDCs. The texture of base soil was in the range of drill cuttings summarized in Table 2.1. Base soil pH, electrical conductivity (EC), organic matter, total carbon (TC), total nitrogen (TN) and available phosphorus (PO_4-P) were analyzed.

3.2 Chemicals and instruments

Decane (nC10; >99% pure), hexadecane (nC16; >99% pure), and tetratriacontane (nC34; >99% pure) used as standard substances for GC analysis were purchased from Sigma-Aldrich. Dichloromethane (DCM) (>99% pure; Sigma-Aldrich) and hexane (>99% pure; Sigma-Aldrich) were used for the PHCs extraction and clean-up processes from the drill cuttings. Ottawa sand (#30-40, Fisher Scientific) was used to enhance the LTTD process of drill cuttings remediation.

A compact 1100 °C vacuum tube furnace (GSL-1100X, MTI Co., USA) was used as the thermal reactor for LTTD treatment, and its specifications are listed in Table 3.1. A plug power meter (RR-YU-POHJU-LO, RioRand Advanced Technology, Canada) with 0-1800 W of Wattage display was used to monitor the energy consumption during the OBDCs

remediation using LTTD treatment. An orbital shaker (C2 Platform Shaker, New Brunswick Scientific Co., USA) was used for mechanical extraction of TPH. A rotary evaporator (RE 400, Yamato Scientific America Inc., USA) was used to concentrate petroleum hydrocarbon extracts.

Table 3.1 Summary of thermal reactor specifications

Parameter	Value
Power, W	1500
Operating voltage	AC 110/220V single phase, 50/60 Hz
Max. temperature, °C	1100 (1000 continuous)
Temperature Accuracy, °C	± 1
Max. heating rate, °C min^{-1}	20 (10 suggested)
Heating zone length, mm	300
Constant temperature zone, mm	80
Temperature control	30 segments programmable digital controller with PID function and overheating and overload protection
Vacuum level, Pa	1.0×10^3

3.3 Artificial OBDCs

The diesel used in this study was obtained from Husky Energy Light Oil Refinery in Prince George, British Columbia, Canada. Sodium chloride (NaCl) was used to achieve certain chloride content in the drill cuttings. Based on previous study (Al-Ansary and Al-Tabbaa, 2007) and the summarized physical characteristics data of North Sea and Red Sea drill cuttings shown in Table 2.1, two OBDCs with different concentrations of PHCs were

synthetized in this study, and the properties of artificial OBDCs were shown in Table 3.2. Most of the heavy metals from geologic formations associated with drill cuttings are in immobile forms and not bioavailable. Therefore, PHCs were as the only study contaminants in this thesis and heavy metals were not mixed into the artificial OBDCs.

The hexane/diesel solutions with different amounts of diesel were mixed completely with the base soil until the soil was just saturated with the liquid. The artificial OBDCs with low and high content of oil (called LOC and HOC, respectively) were formed (Figure 3.1). The liquid/soil mixtures were kept stirring for 30 min, and the hexane and light oil fraction were allowed to evaporate in the fume hood for one week. Water content in OBDCs must be decreased prior to LTTD to reduce the treatment cost. The dry drill cuttings samples were manually blended again to obtain homogeneous oil distribution. The TPH content of artificial OBDCs were subsequently analyzed and the obtained drill cuttings were stored in glass bottles in the fridge at 4 °C. PHCs were quantified by analyzing concentrations of PHC fractions - F2 (PHCs from nC10 to nC16), F3 (PHCs from nC16 to nC34), and F4 (PHCs from nC34 to nC50) (CCME, 2001).

Table 3.2 Properties of the OBDCs

Property		Value
Chloride content, %		2.03
Hydrocarbon content in the LOC, mg kg^{-1}	F2 *	15248.79 ± 210.92
	F3 *	22897.91 ± 136.40
	TPH *	38146.70 ± 100.23
Hydrocarbon content in the HOC, mg kg^{-1}	F2 *	20870.15 ± 206.52
	F3 *	44813.87 ± 682.15
	TPH *	65684.012 ± 804.05

* Indicates a significant difference at $p < 0.05$ (two-tailed) between LOC and HOC samples

(a)  (b) 

Figure 3.1 Artificial LOC (a) and HOC (b)

3.4 Experimental apparatus and procedures for LTTD

OBDCs samples were treated under simulating LTTD conditions using a bench-scale apparatus with the schematic shown in Figure 3.2. The system consists of an input gas transport part, a compact vacuum tube furnace (thermal reactor), and a quartz cylindrical tube (inner diameter: 50mm, length: 450mm) where the small quartz container with samples were

placed. The gas output section was connected to n-hexane traps in a cooling tank. Figure 3.3 shows the LTTD system in the laboratory fume hood.

During the experiments, the quartz tube was purged with a constant nitrogen flow of 100 mL min^{-1} at a pressure of 1 atm for 10 min to create an oxygen free environment. The thermal reactor was heated at the rate of 10 °C min^{-1} to achieve assigned temperature before starting remediation. The oxygen free environment was kept to avoid combustion. Keeping constant temperature, 10.00 g of dry OBDCs sample evenly mixed with Ottawa sand (expressed by sand/OBDCs mass mixing ratio, S/C) was placed inside the quartz cylindrical tube to be heated under the conditions shown in Table 3.3. Following the thermal reactor, hexane traps were plugged to the glass tube to clean the volatilized PHCs in the exhaust and avoid secondary pollution to air. After treatment, samples were removed from the apparatus, cooled at room temperature (25 °C) and stored in the dark at 4 °C prior to analyzing. A full experimental design with 4 factors and 2 duplicates was used to investigate the effects of different factors on the desorption kinetics, with a total experimental run number of 192 (4 × 3 × 2 × 4 × 2). The LTTD procedure was carried out in duplicates and the mean values of TPH in the residual were obtained for selected temperatures and OBDCs.

Petroleum hydrocarbons removal efficiency (R_e) was calculated using the total mass loss of hydrocarbons:

$$R_e = 100\% - \frac{C \times W}{C_0 \times W_0} \times 100\% \quad (1)$$

where C_0 and W_0 are the initial hydrocarbons concentration (mg kg^{-1}) and weight (g) of OBDCs before the LTTD, C and W are the residual hydrocarbons concentration (mg kg^{-1})

and weight (g) of OBDCs after the LTTD. 10.00 g (W_0) of dry OBDCs sample was used for each experiment.

Table 3.3 Influencing factors and their values used in the treatment

Parameters	Values [a]
A: Treatment temperature, °C	150 (1), 200 (2), 250 (3), 300 (4)
B: Sand/OBDCs mixing ratio (S/C)	0 (1), 0.5 (2), 1 (3)
C: Initial TPH content, %	3.8 (1), 6.6 (2)
D: Treatment time, min	5 (1), 10 (2), 20 (3), 30 (4)

a. Real values and coded levels (in parentheses) of experimental factors

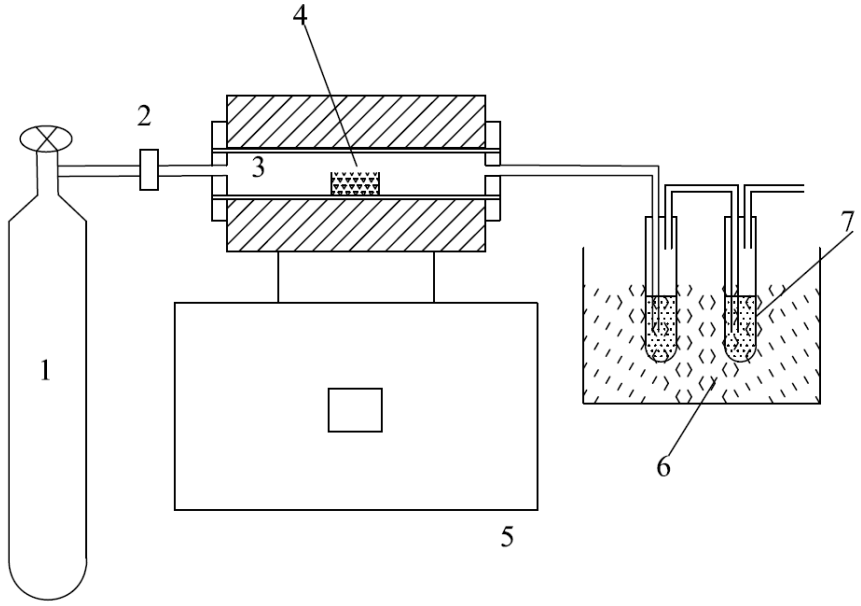


Figure 3.2 Schematics of LTTD system. (1) nitrogen cylinder; (2) flow & pressure regulator; (3) quartz tube; (4) sample; (5) compact vacuum tube furnace; (6) cooling tank (ice-water); (7) hexane trap

Figure 3.3 Bench-scale LTTD system in the laboratory fume hood

3.5 Kinetic data modelling

It has been demonstrated that thermal desorption of petroleum hydrocarbons in soil follows exponential kinetic decay in nature. Thus, the residual PHCs content versus treatment duration curves could be fitted using nonlinear least-squares regression to an exponential decay function (Eq. 2) (Smith et al, 2001; Falciglia et al., 2011). In this study, the total mass (mg) of PHCs in OBDCs instead of oil concentration (mg kg^{-1}) was used for the calculation of oil removal efficiency and modeling, because the oil concentration changes accordingly with water content and sand addition. This can avoid testing for water content of each treated OBDCs sample and represent the actual oil removal of the treatment.

$$w = w_0 e^{-kt^n} \quad (2)$$

where $w = C \times W$ represents the mass of residual contaminants (mg) in OBDCs after a treatment time t (min), $w_0 = 10C_0$ is the initial mass of contaminants (mg), k is the decay rate

of the function (min $^{-1}$), and n represents the shape of the decay curve. Both parameters k and n are functions of the thermal desorption temperature. Parameter n shows the effects on the decay in three ways: the decay is purely exponential if n=1, and the decay is faster than exponential if n>1, while the decay is slower than exponential if n<1.

To determine the desorption rate in terms of the residence time, Eq. (2) can be expressed as:

$$-dw/dt = wknt^{n-1} \quad (3)$$

Rearranging Eq. (2), we get an expression for t in terms of TPH content:

$$t = (-\frac{1}{k} ln \frac{w}{w_0})^{1/n} \quad (4)$$

By substituting Eq. (4) into Eq. (3), we yield an expression for the desorption rate in terms of the residual contaminant content:

$$-dw/dt = wkn[-\frac{1}{k} ln \frac{w}{w_0}]^{(n-1)/n} \quad (5)$$

By using a data analysis and graphing software Origin 9, residual F2, F3 and TPH results obtained under each temperature with time were fitted using the exponential decay kinetic model expressed by Eq. (2). Model parameters k and n for LOC and HOC with different sand/OBDCs ratio at different final temperatures were calculated and the corresponding correlation coefficient (adjusted R^2) was evaluated. With the calculated values of k and n, we can assess the effects of each factor on the TPH removal efficiency in the OBDCs remediation using LTTD. The temperature and time of treatment required to reach specific remediation levels can then be identified for OBDCs with known initial F2, F3 and TPH content. The desorption rate (-dw/dt) from Eq. (5) would be plotted as a function of residual

TPH content (w) in the OBDCs, which could provide the immediate desorption rate of each model with the desorption of PHCs (Smith et al, 2001). It can visually indicate the impacts of each factor on the desorption rate of LTTD system.

3.6 Energy consumption

A power meter was plugged with the furnace to record the energy consumption (E, kwh) during the heating up and heat sustaining procedures of each LTTD treatment. The curves of energy consumption at each temperature and sand/OBDCs mixing ratio for LOC and HOC remediation were illustrated with kinetic modeling curves. The optimal treatment temperature and time for OBDCs with known initial TPH concentration can then be obtained to achieve specific management levels with minimum energy consumption (Table 3.4).

Table 3.4 Canadian recommended management limits for each PHC fraction (CCME, 2008)

Soil Texture	Management limit for each PHC fraction (mg kg $^{-1}$)			
	F1	F2	F3	F4
Coarse-grained soil	700	1000	2500 (ag/res) 3500 (com/ind)	10000
Fine-grained soil	800	1000	3500(ag/res) 5000(com/ind)	10000

ag: agricultural, res: residential, com: commercial, ind: industrial

3.7 Extraction of petroleum hydrocarbons from OBDCs

According to McMillan (2008) and Alinnor et al. (2014), mechanical shaking method is comparable in accuracy to the Soxhlet extraction recommended by CCME (2001). 1-2 g of dry OBDCs samples were added to 50 mL of centrifuge tubes with about 10 mL of DCM,

followed by shaking on an orbital shaker for mechanical extraction at 150 rpm for 30 minutes. Samples of the organic phase were separated and transferred into 40 mL clean vials after being centrifuged at 4500 rpm for 5 min. The extraction was conducted three times, with about 30 mL of extraction solution collected.

The extraction solution was transferred into a glass column for cleanup (CCME, 2001) (Figure 3.4). The column was packed with approximately 6 cm (in length) of silica gel (activated at 110 °C for 12 hours) and 2 cm of anhydrous sodium sulfate (dried at 400 °C for 12 hours) and rinsed with 20 mL of 1:1 hexane/DCM solvent. Another 20 mL of solvent (1:1 hexane/DCM) was poured to elute the column after the extraction solution passed through. The extraction solution was collected by a conical flask placed under the column and then evaporated by a rotary evaporator to reduce the volume to 1-2 mL. After that, the residue was transferred into a 10 mL of volumetric flask with hexane to reach the final volume of 10 mL. 1.5 mL of sample was then used for GC analysis.

Figure 3.4 Silica gel column clean-up for petroleum hydrocarbons extracts

3.8 Analysis and calculation of petroleum fractions and TPH

Gas Chromatograph with flame ionization detector (GC-FID) was used for TPH analysis. The parameters for GC analysis are set as following: 30 m metal column with 0.32 mm ID; injector temperature at 270 °C; detector temperature at 280 °C; nitrogen as carrier gas with a constant flow rate at 7.5 mL min^{-1}; oven temperature starting at 70 °C for 2 min, gradually increasing to 150 °C at 5 °C min^{-1}, rising to 270 °C at 10 °C min^{-1} and holding for 25 minutes. The decane (nC10), hexane (nCl6), and tetratriacontane (nC34) were used as standard substances for the determination of petroleum hydrocarbons fractions. Calibration and retention time marking for the C10 to C34 hydrocarbons using nC10, nC16 and nC34 hydrocarbons dissolved in hexane were performed before analysis. Calibration is based on the integration of area under the chromatogram between retention time markers.

A response factor (RF) for each of the hydrocarbon standard alkanes (nC10, nC16 and nC34) in the calibration runs was calculated, and the average of all these response factors was obtained (RF_{ave}), based on equations (6) and (7).

$$\mathrm{RF} = \frac{A_{n-alk}}{C_{n-alk}} \tag{6}$$

$$RF_{ave} = \frac{sum\ of\ individual\ RF\ values}{number\ of\ RF\ values\ used} \tag{7}$$

Where $A_{n\text{-}alk}$ is the area under the individual n-alkane peak and $C_{n\text{-}alk}$ is the concentration of individual n-alkane standard.

RF_{ave} was then used to calculate the petroleum fractions (F2 and F3) and TPH in each sample via following equations:

$$C_{F2}(mg\ kg^{-1}) = \frac{A_{C10-C16} \times V \times F}{RF_{ave} \times W_d} \tag{8}$$

$$C_{F3}(mg\ kg^{-1}) = \frac{A_{C16-C34} \times V \times F}{RF_{ave} \times W_d} \quad (9)$$

$$TPH(mg\ kg^{-1}) = C_{F2} + C_{F3} \quad (10)$$

Where $A_{C10-C16}$ and A_{C16-34} are the integration of all area counts from the apex of C10 to C16 peak and the integration of area from C16 to C34; V (mL) is the final volume of sample extract; F represents the dilution factor applied to each sample extract, and W_d (g) is the dry weight of sample taken.

Chapter 4 Results and discussion

4.1 Changes in physicochemical properties of OBDCs

The properties of base soil used to synthetize OBDCs before and after LTTD at 300 °C for 20 min were analyzed as shown in Table 4.1. An independent samples T test was conducted by a statistical analysis software IBM SPSS 18. As was seen from the results, F2 fraction in HOC after treatment was completely removed and F3 fraction was nearly removed (99.57%). TPH was barely left in the drill cuttings after thermal desorption. The textural class of base soil for artificial OBDCs was silt loam, and it was changed to clay loam during the treatment. After LTTD treatment, the average content of sand (0.02 - 2 mm) increased from 21.23% to 40.31%, while that of silt (0.02–0.002 mm) decreased from 50.82% to 27.94%. This is in agreement with Terefe et al. (2008) who suggested that silt- and clay-sized particles formed sand-sized aggregates through a cementing effect at thermal temperatures of 300-500 °C. However, a lower temperature (250 °C) or shorter thermal treatment duration (10 min) may not significantly change the composition of soils as observed by Yi et al. (2016). The pH of HOC after LTTD was increased ($p < 0.05$) and closer to neutral, as compared to base soil and HOC before treatment. It was reported that heating could enhance the pH values of acidic soil (Yusiharni and Gilkes, 2012). This could be explained by the loss of organic acids and the release of alkaline cations by the heating effect (Arocena and Opio, 2003). In addition, Terefe et al. (2008) indicated that pH values increased with heating temperature in acidic soils but decreased in the alkaline soils at temperatures above 300 °C. The EC of OBDCs after thermal desorption slightly increased, but the difference was not significant ($p > 0.05$). This may also indicate the release of alkali cations, and it can be contributed by the consequent liberation of ions in the complex with

organics, as a result of heating (Terefe et al., 2008). As compared to the base soil, the organic matter and TN contents in HOC after LTTD decreased by 18.51 % ($p < 0.001$) and 3.66 % ($p > 0.05$), respectively. This is in agreement with Yi et al. (2016) who found that due to heating, the loss of gaseous oxides of C and N generally causes the decrease of organic matter and nitrogen levels with increasing temperature. However, the TC and available phosphorus (PO_4-P) contents after LTTD significantly increased by 65.63% ($p < 0.001$) and 69.68% ($p < 0.05$), respectively, as compared to those in base soil (i.e., 0.96 % and 45.58 mg kg^{-1}). This may be because the organic phosphorous and PHCs can be converted to inorganic forms, increasing the available PO_4-P and inorganic carbon (Yusiharni and Gilkes, 2012). Soil fertility and the C/N ratio would be affected by the changes of nitrogen and phosphorus concentration in soil. Increased available phosphorous content in soil can benefit plant growth if other soil properties are unchanged (Yi et al., 2016). Compared to complete removal of PHCs from OBDCs, less treatment time (8.5 min) for HOC with S/C mixing ratio of 1.0 at 300 °C will be more beneficial. This can maximally keep soil health and achieve management limits of drill cuttings (introduced in section 4.7).

Table 4.1 Base soil properties and physicochemical characteristics of HOCs before and after LTTD treatment at 300 °C for 20 min

Properties		Base soil	Low-temperature thermal desorption	
			Before	After
pH (soil:water=1:2)		5.15 ± 0.01 [a]	5.31 ± 0.04 [b]	5.68 ± 0.01
EC (soil:water=1:2), ms cm^{-1}		16.82 ± 0.02	13.74 ±1.77	17.50 ± 0.33
Organic matter, % *		3.62 ± 0.17 [A]	15.33 ±0.18 [B]	2.95 ±0.15
TC, % *		0.96 ± 0.01 [A]	11.40 ± 0.20 [b]	1.59 ± 0.01
TN, % *		0.0546 ± 0.0009	0.0555 ± 0.0029	0.0526 ± 0.0012
PO_4-P, mg kg^{-1} *		45.58 ± 0.65 [a]	55.69 ± 4.20 [b]	77.34 ± 2.20
Particle size *	Sand, %	21.23 [c]	34.06 [c]	40.31
	Silt, %	50.82 [c]	41.25 [c]	27.94
	Clay, %	27.95 [c]	24.70 [c]	31.75
F2		nd [c]	20930.76 ± 251.51 [b]	0 ± 0
F3		nd [c]	44616.95 ± 835.46 [b]	190.33 ± 21.55
TPH		nd [c]	65547.71 ± 1086.98 [b]	190.33 ± 21.55

* All data were analyzed by the Analytical Chemistry Laboratory of the BC Ministry of Environment

a & A indicates a significant difference between base soil and HOC after LTTD treatment at $p < 0.05$ and $p < 0.001$ (two-tailed), respectively; b & B indicates a significant difference between HOCs before and after LTTD treatment at $p < 0.05$ and $p < 0.001$ (two-tailed).

nd: not determined

c. not applicable

4.2 Kinetics of F2 removal from OBDCs with LTTD system

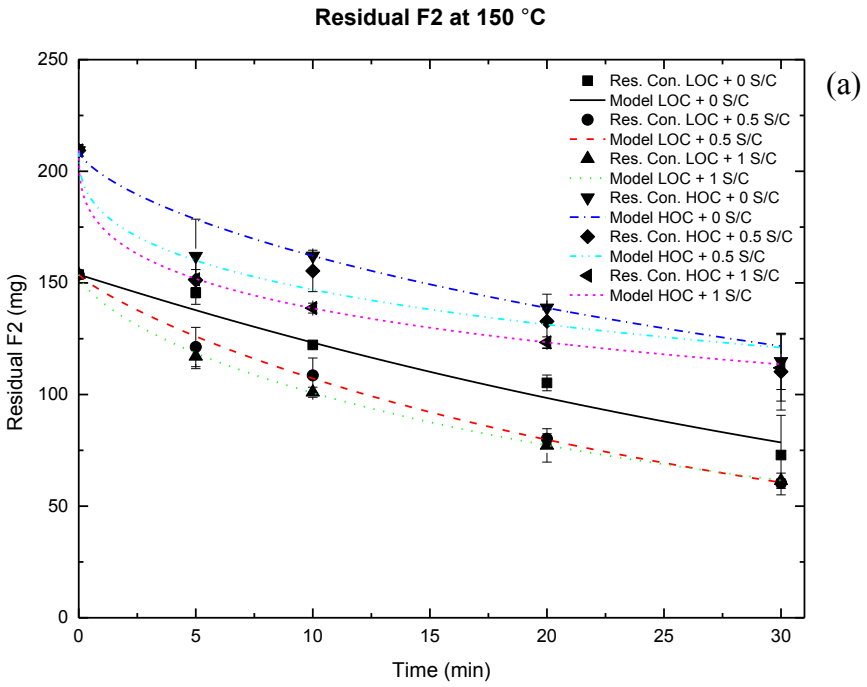
Fig. 4.1 shows the kinetics of residual F2 in LOCs and HOCs with treatment time at a S/C mixing ratio of 0, 0.5 and 1.0 and treatment temperatures of 150, 200, 250 and 300 °C, respectively. As expected, F2 content in all the OBDCs samples after thermal treatment decreased with treatment time. The rate of F2 desorption also improved with the increase of treatment temperature.

The F2 removal rates of LTTD treatment at 150 and 200 °C were relatively low. The F2 contaminants in both LOCs and HOCs were not completely removed at the maximum treatment time (30 min) at 150 and 200 °C, although 40-60% and 80-90% of F2 could be removed at each temperature, respectively. However, the removal rates for F2 treated at 250 and 300 °C were fairly high, reaching nearly 100% removal efficiency for all the treated OBDCs samples after 20 and 10 min, respectively. Similar to the F2 removal at 150 and 200 °C, further contaminant removal at 250 and 300 °C occurred at very low rates after about 15 and 7 min of treatment, respectively. This is probably due to the two different phases in thermal treatment that change slope in the kinetic curves. During the first phase, the contaminants are rapidly volatilized from the soil particle surface. However, the evaporation rate is restrained by internal diffusion phenomena at the later phase (Keyes and Silcox, 1994). In addition, it was found that the addition of sand to the OBDCs could promote the removal rate of F2, especially at low temperatures (150 and 200 °C) or in HOCs.

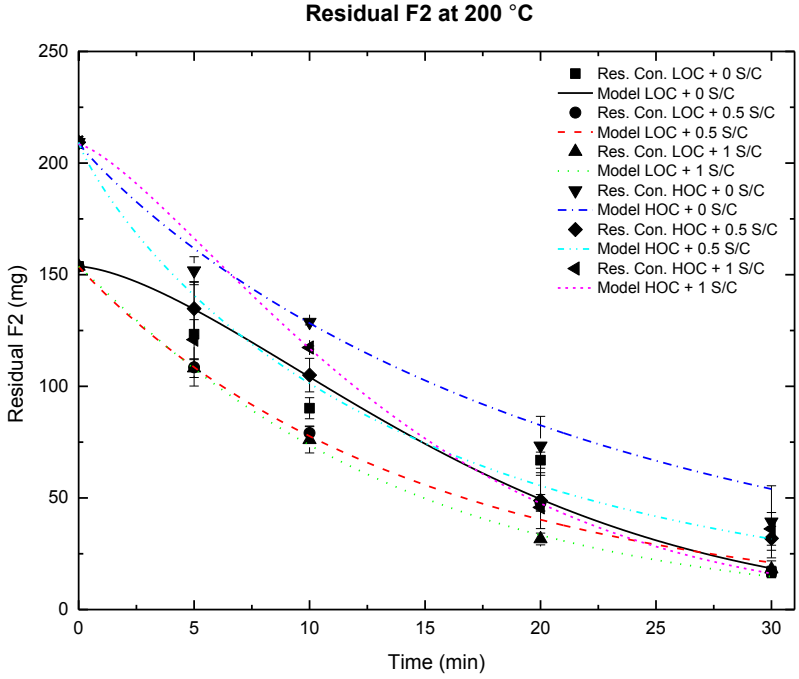
The data of residual F2 were fitted to Eq. (2), and the model parameters (k and n) as well as the adjusted R^2 values are shown in Table 4.2. The nonlinear least-squares exponential kinetic model exhibited a great correlation (adjusted $R^2 > 0.9$) with the experimental data for all the treated OBDCs samples. Tests of between-subjects effects for k and n values were

also analyzed using IBM SPSS 18 as shown in Table 4.3. The shapes (n) of the decay curve were strongly correlated to treatment temperature since p values were all less than 0.001, while the decay rates (k) did not show significant difference ($p = 0.18$), indicating that the increase of treatment temperature improved the F2 removal rates mainly by increasing n values. Both k and n values were statistically correlated to S/C ratios ($p < 0.05$), while there was no statistically significant difference in k and n values between models of LOC and HOC ($p > 0.05$). Generally, the addition of sand to the OBDCs sample increased n values and thus improved the F2 removal rates. In addition, when considering k and n values, no significant interaction was found between any two factors, including treatment temperature (A), S/C ratio (B) and initial TPH content (C), as all p values of A*B, A*C and B*C were greater than 0.05.

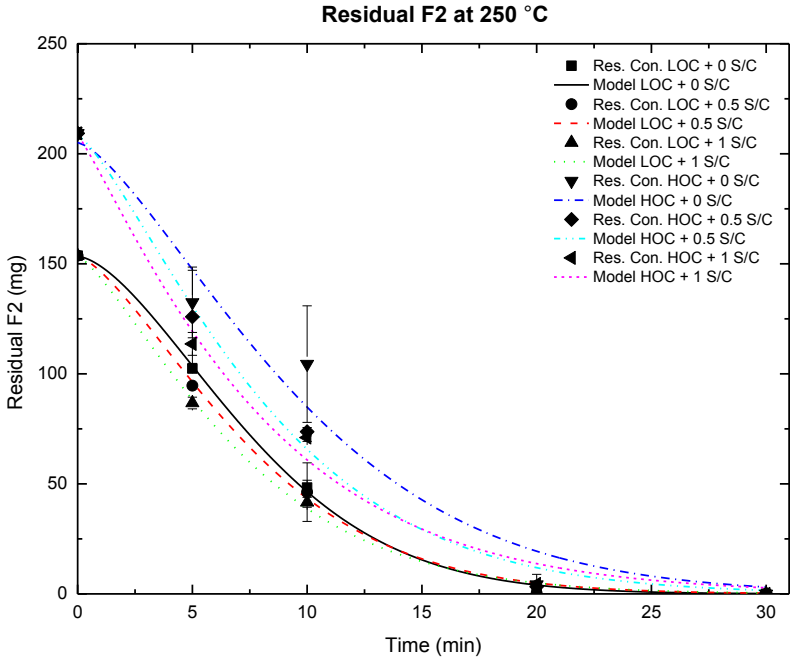
With known initial F2 content in OBDCs, treatment time under specific treatment conditions to reach Canadian F2 management limits (1000 mg kg^{-1} for industrial fine-grained soil) (Table 3.4) could be assessed using Eq. (4). Such information can be used for optimizing energy efficiency and the cost of a thermal remediation process. According to Falciglia et al. (2011), an average of approximately 0.22 \$ $°C^{-1}$ min^{-1} could be saved for a typical 20 t/h rotary kiln system supplied by diesel fuel. Therefore, even a small adjustment of the treatment temperature or time could have significant impacts on the remediation costs.


Residual F2 at 150 °C
Residual F2 (mg)
Time (min)
Res. Con. LOC + 0 S/C
Model LOC + 0 S/C
Res. Con. LOC + 0.5 S/C
Model LOC + 0.5 S/C
Res. Con. LOC + 1 S/C
Model LOC + 1 S/C
Res. Con. HOC + 0 S/C
Model HOC + 0 S/C
Res. Con. HOC + 0.5 S/C
Model HOC + 0.5 S/C
Res. Con. HOC + 1 S/C
Model HOC + 1 S/C

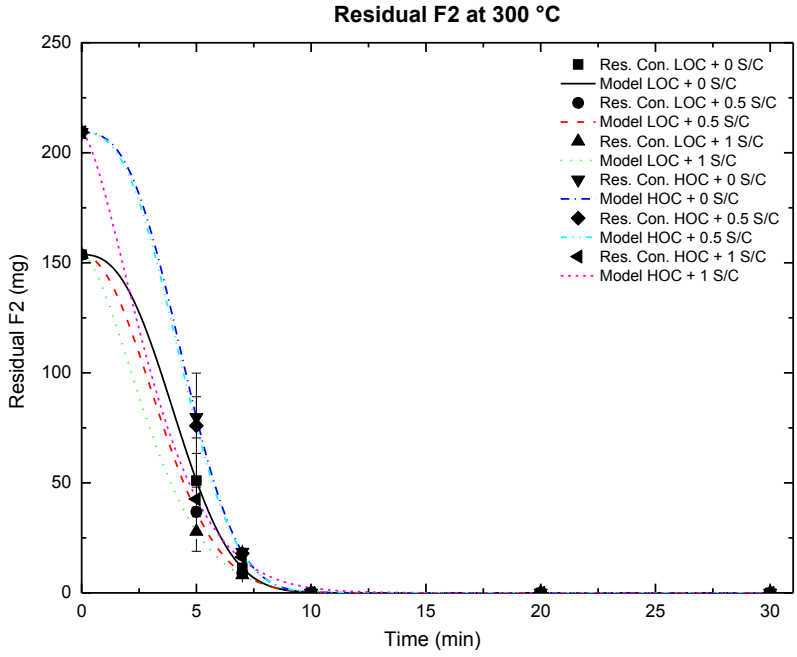
(a)


Residual F2 at 200 °C
Residual F2 (mg)
Time (min)
Res. Con. LOC + 0 S/C
Model LOC + 0 S/C
Res. Con. LOC + 0.5 S/C
Model LOC + 0.5 S/C
Res. Con. LOC + 1 S/C
Model LOC + 1 S/C
Res. Con. HOC + 0 S/C
Model HOC + 0 S/C
Res. Con. HOC + 0.5 S/C
Model HOC + 0.5 S/C
Res. Con. HOC + 1 S/C
Model HOC + 1 S/C

(b)



(c)



(d)

Figure 4.1 Residual F2 by mass and kinetic model curves for LOCs and HOCs at a S/C mixing ratio of 0, 0.5 and 1.0 under different treatment temperatures, (a) 150 °C, (b) 200 °C, (c) 250 °C, and (d) 300 °C

Table 4.2 Desorption parameters k (min $^{-1}$) and n and adjusted R^2 of the kinetic model of F2 removal under treatment temperature of 150, 200, 250 and 300 °C for all the tested OBDCs samples

T(°C)	LOC with S/C of 0				LOC with S/C of 0.5				LOC with S/C of 1.0			
	k	n	Adjusted R^2	Prob>F	k	n	Adjusted R^2	Prob>F	k	n	Adjusted R^2	Prob>F
150	0.0215	1.0125	0.9802	<0.001	0.0495	0.8629	0.9998	<0.001	0.0837	0.7032	0.9999	<0.001
200	0.0112	1.5427	0.9957	<0.001	0.0726	0.9732	0.9988	<0.001	0.0648	1.0552	0.9992	<0.001
250	0.0295	1.6082	0.9979	<0.001	0.0457	1.4412	0.9962	<0.05	0.0665	1.3158	0.9963	<0.05
300	0.0180	2.5578	1.0000	<0.001	0.0527	2.0506	1.0000	<0.001	0.1194	1.6519	1.0000	<0.001
T(°C)	HOC with S/C of 0				HOC with S/C of 0.5				HOC with S/C of 1.0			
	k	n	Adjusted R^2	Prob>F	k	n	Adjusted R^2	Prob>F	k	n	Adjusted R^2	Prob>F
150	0.0527	0.6852	0.9975	<0.001	0.1411	0.3988	0.9670	<0.001	0.1798	0.3602	1.0000	<0.001
200	0.0576	0.9284	0.9911	<0.001	0.0977	0.8710	0.9986	<0.001	0.0255	1.3550	0.9785	<0.05
250	0.0337	1.4184	0.9455	<0.05	0.0564	1.3106	0.9893	<0.05	0.0885	1.1433	0.9846	<0.05
300	0.0118	2.7377	1.0000	<0.001	0.0147	2.6327	1.0000	<0.001	0.1397	1.5086	0.9997	<0.001

Table 4.3 Tests of between-subjects effects for k (min $^{-1}$) and n of F2 desorption kinetics model

Source	Dependent variable	Type III sum of squares	df	Mean square	F	Prob>F
Corrected Model	k	.043[a]	17	.003	3.575	.061
	n	9.226[b]	17	.543	10.773	.004
Intercept	k	.098	1	.098	140.060	.000
	n	43.000	1	43.000	853.578	.000
A: Treatment	k	.005	3	.002	2.273	.180
temperature	n	7.318	3	2.439	48.421	.000
B: Sand/OBDCs	k	.018	2	.009	12.689	.007
mixing ratio (S/C)	n	.727	2	.363	7.215	.025
C: Initial TPH	k	.003	1	.003	4.155	.088
content	n	.085	1	.085	1.680	.243
A * B	k	.011	6	.002	2.733	.123
	n	.787	6	.131	2.605	.135
A * C	k	.006	3	.002	2.658	.142
	n	.263	3	.088	1.741	.258
B * C	k	3.450E-5	2	1.725E-5	.025	.976
	n	.046	2	.023	.459	.652
Error	k	.004	6	.001		
	n	.302	6	.050		
Total	k	.145	24			
	n	52.529	24			
Corrected Total	k	.047	23			
	n	9.528	23			

a. R Squared = .910 (Adjusted R Squared = .656)

b. R Squared = .968 (Adjusted R Squared = .878)

* Denotes the interaction between two factors

4.3 Kinetics of F3 removal from OBDCs treated with LTTD

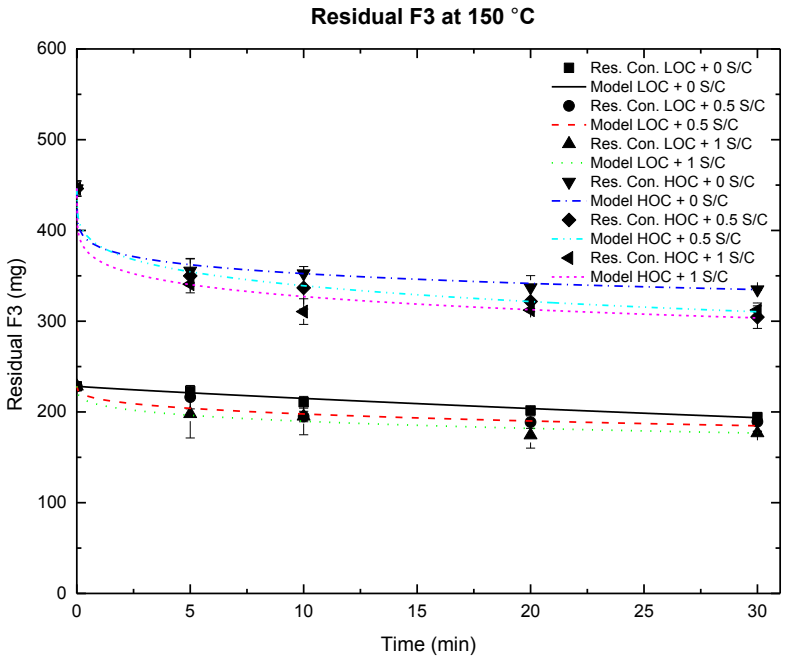
The kinetics of residual F3 in LOCs and HOCs with treatment time at a S/C mixing ratio of 0, 0.5 and 1.0 under the treatment temperature of 150, 200, 250 and 300 °C, respectively, were fitted and shown in Fig. 4.2. Similar to F2 removal kinetics, residual F3 in all the treatments decreased with treatment time, while the removal rates increased with treatment temperature. However, the desorption rate of F3 under each temperature was much slower than that of F2 under the same temperature.

The F3 removal rates for all treatments at 150 and 200 °C were fairly low, and the kinetics curves became nearly flat after 5 min of treatment. Less than 40% of F3 contaminants were removed from both LOCs and HOCs after 30 min of LTTD treatment at 150 and 200 °C. However, the F3 removal rates at 250 and 300 °C greatly increased as compared to those at lower treatment temperature. Almost 90% and 100% of F3 were removed at 250 and 300 °C after 30 min of treatment, respectively.

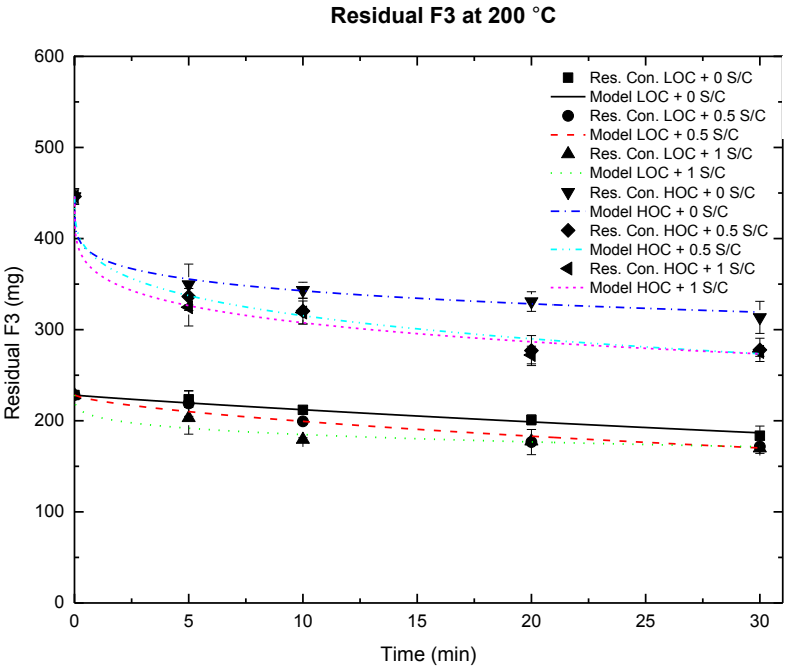
As observed from the parameters (k and n) and adjusted R^2 values for F3 removal kinetics curves (Table 4.4), the nonlinear least-squares exponential kinetics model presented an excellent correlation (adjusted R^2 >0.96) with the experimental data for all the treated OBDCs samples. Based on the tests of between-subjects effects shown in Table 4.5, the treatment temperature could significantly affect k values ($p < 0.05$), and highly significantly impact n values ($p < 0.001$). The treatment temperature enhanced the F3 removal rates mainly by increasing n values. Both k and n values were statistically correlated to S/C ratio ($p < 0.05$). However, differing from F2 removal kinetics, both k and n values were highly significantly different between LOC and HOC models ($p < 0.001$). It was found that the increase of initial TPH content increased n values but decreased k values. Furthermore, a

significant interaction between treatment temperature and initial TPH content was found when considering k values, as p value of A*C was less than 0.05. The effect of S/C mixing ratio on both k and n values significantly differed between LOC and HOC since the p values for B*C were less than 0.05.

To optimize remediation efficiency and the cost of a LTTD process, treatment time at specific thermal temperature and S/C mixing ratio to achieve Canadian F3 management limits (i.e., 5000 mg kg^{-1} for industrial fine-grained soil) (Table 3.4) could be evaluated using Eq. (4) with known initial F3 content in OBDCs.


Residual F3 at 150 °C
Residual F3 (mg)
Time (min)
Res. Con. LOC + 0 S/C
Model LOC + 0 S/C
Res. Con. LOC + 0.5 S/C
Model LOC + 0.5 S/C
Res. Con. LOC + 1 S/C
Model LOC + 1 S/C
Res. Con. HOC + 0 S/C
Model HOC + 0 S/C
Res. Con. HOC + 0.5 S/C
Model HOC + 0.5 S/C
Res. Con. HOC + 1 S/C
Model HOC + 1 S/C

(a)


Residual F3 at 200 °C
Residual F3 (mg)
Time (min)
Res. Con. LOC + 0 S/C
Model LOC + 0 S/C
Res. Con. LOC + 0.5 S/C
Model LOC + 0.5 S/C
Res. Con. LOC + 1 S/C
Model LOC + 1 S/C
Res. Con. HOC + 0 S/C
Model HOC + 0 S/C
Res. Con. HOC + 0.5 S/C
Model HOC + 0.5 S/C
Res. Con. HOC + 1 S/C
Model HOC + 1 S/C

(b)

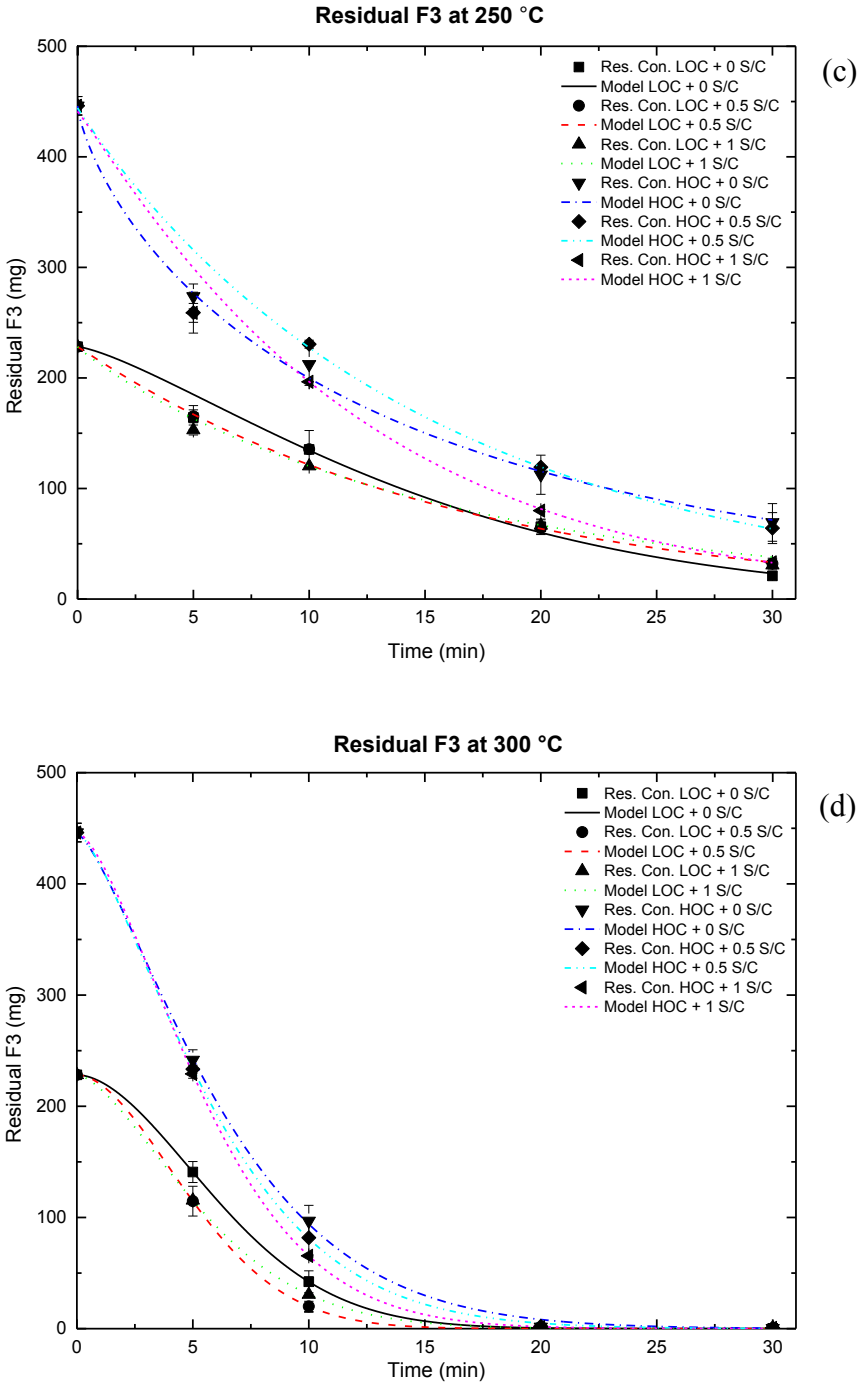


Figure 4.2 Residual F3 by mass and kinetics model curves for LOCs and HOCs at S/C mixing ratio of 0, 0.5 and 1.0 under different treatment temperatures, (a) 150 °C, (b) 200 °C, (c) 250 °C, and (d) 300 °C

Table 4.4 Desorption parameters k (min^{-1}) and n and adjusted R^2 of kinetics model of F3 removal at temperature of 150, 200, 250 and 300 °C for all the tested OBDCs samples

T(°C)	LOC with S/C of 0				LOC with S/C of 0.5				LOC with S/C of 1.0			
	k	n	Adjusted R^2	Prob>F	k	n	Adjusted R^2	Prob>F	k	n	Adjusted R^2	Prob>F
150	0.0074	0.9110	0.9926	<0.001	0.0635	0.3535	0.9658	<0.001	0.0936	0.2957	0.9993	<0.001
200	0.0089	0.9173	0.9956	<0.001	0.0268	0.7040	0.9985	<0.001	0.1112	0.2776	0.9939	<0.001
250	0.0245	1.3342	0.9981	<0.001	0.0607	1.0168	0.9993	<0.001	0.0742	0.9367	0.9994	<0.001
300	0.0263	1.8079	1.0000	<0.001	0.0367	1.8219	1.0000	<0.001	0.0556	1.5568	1.0000	<0.001
T(°C)	HOC with S/C of 0				HOC with S/C of 0.5				HOC with S/C of 1.0			
	k	n	Adjusted R^2	Prob>F	k	n	Adjusted R^2	Prob>F	k	n	Adjusted R^2	Prob>F
150	0.1561	0.1790	0.9981	<0.001	0.1527	0.2543	0.9973	<0.001	0.1976	0.1962	0.9830	<0.001
200	0.1603	0.2165	0.9959	<0.001	0.1690	0.3125	0.9906	<0.001	0.2092	0.2501	0.9806	<0.001
250	0.1428	0.7501	0.9983	<0.001	0.0715	0.9714	0.9907	<0.001	0.0701	1.0621	0.9994	<0.001
300	0.0681	1.3594	0.9992	<0.001	0.0677	1.4016	0.9999	<0.001	0.0571	1.5266	1.0000	<0.005

Table 4.5 Tests of between-subjects effects for k (min $^{-1}$) and n of F3 desorption kinetics model

Source	Dependent variable	Type III sum of squares	df	Mean square	F	Prob>F
Corrected Model	k	.081 [a]	17	.005	13.201	.002
	n	6.855 [b]	17	.403	39.305	.000
Intercept	k	.186	1	.186	516.917	.000
	n	17.362	1	17.362	1692.419	.000
A: Treatment temperature	k	.017	3	.006	15.329	.003
	n	5.735	3	1.912	186.353	.000
B: Sand/OBDCs mixing ratio (S/C)	k	.005	2	.003	7.337	.024
	n	.118	2	.059	5.757	.040
C: Initial TPH content	k	.036	1	.036	100.886	.000
	n	.497	1	.497	48.448	.000
A * B	k	.006	6	.001	2.670	.129
	n	.094	6	.016	1.520	.312
A * C	k	.012	3	.004	11.425	.007
	n	.033	3	.011	1.087	.424
B * C	k	.005	2	.002	6.286	.034
	n	.377	2	.189	18.388	.003
Error	k	.002	6	.000		
	n	.062	6	.010		
Total	k	.269	24			
	n	24.279	24			
Corrected Total	k	.083	23			
	n	6.916	23			

a. R Squared = .974 (Adjusted R Squared = .900)

b. R Squared = .991 (Adjusted R Squared = .966)

* Donates the interaction between two factors

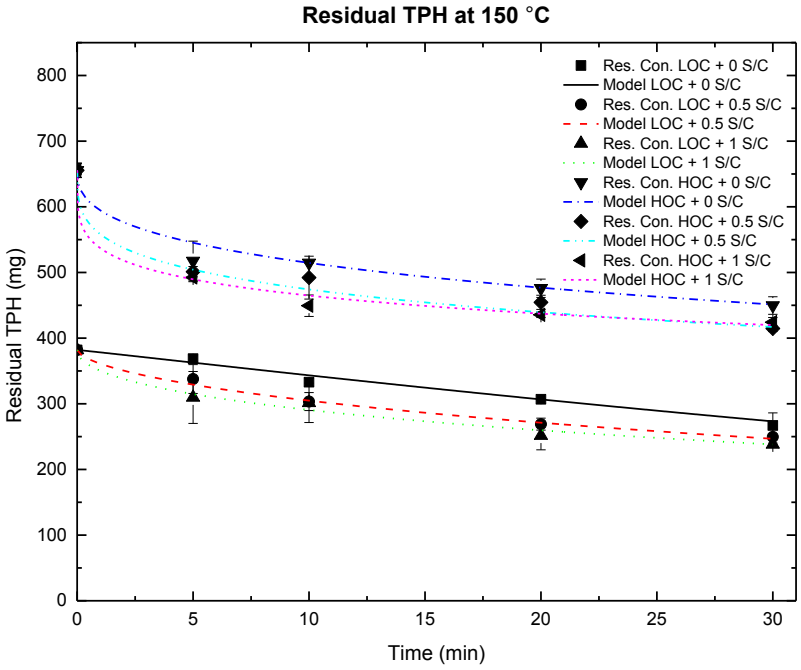
4.4 Kinetics of TPH removal from OBDCs treated with LTTD

The kinetics of TPH removal from LOCs and HOCs at a S/C ratio of 0, 0.5 and 1.0 under the treatment temperatures of 150, 200, 250 and 300 °C, respectively, were shown in Fig. 4.3. It can be seen that the slopes of TPH removal kinetics models were less than those of F2 removal but greater than those of F3 removal, although the TPH desorption kinetics were more similar to that of F3 desorption. Residual TPH in all treatments decreased with treatment time, and the removal rates increased with treatment temperature. Generally, the addition of sand to OBDCs improved the desorption rates of TPH, which is in agreement with Samaksaman et al. (2016a) who showed that a ratio of sand/soil (0.75/1 to 1.5/1) could enhance the elimination of BTEX and PAHs in both fixed bed and fluidized bed reactors.

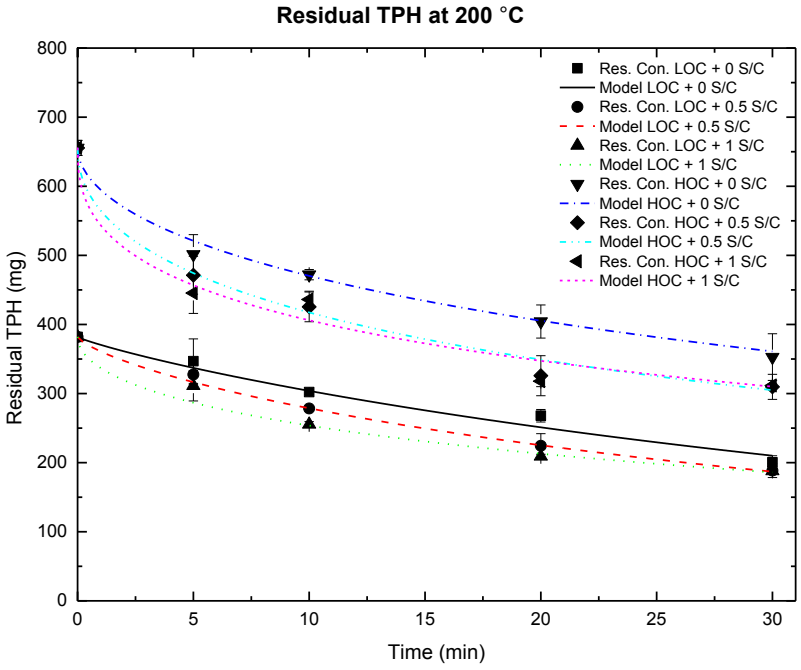
Due to the low F3 removal rates under low thermal treatment temperature (150 and 200 °C), both TPH desorption rate (slope of curves) and removal efficiency for all treatments were also restricted at low levels. For example, less than 50% of TPH was removed from both LOCs and HOCs after 30 min of treatment at 150 and 200 °C, respectively. However, temperatures of 250 and 300 °C were high enough to completely remove all oil contaminants from OBDCs. This is in agreement with Falciglia et al. (2011) who indicated that diesel could be totally eliminated from all sandy, silty and clay soils at 250 and 300 °C. Based on previous literature findings, as compared to the remediation of light hydrocarbons (mainly diesel) in OBDCs, much more time is required to successfully remove recalcitrant contaminants such as organochlorine pesticides (OCPs) and PAHs from soil at low thermal treatment temperature. For example, at 325 °C, 60 min was needed to reach 90% removal for OCPs (about 3000 mg kg^{-1}) contaminated soil (Gao et al., 2013), while at 250 °C, 60 min of treatment could only decrease PAHs from 5% to 2.5% (Smith et al., 2001).

The nonlinear least-squares exponential kinetics model well fitted (adjusted R^2 >0.96) the experimental data for residual TPH, and the parameters of TPH removal kinetics curves were shown in Table 4.6. Table 4.7 presents the tests of between-subjects effects of parameters and influential factors for TPH desorption kinetics models. Similar to F3 removal kinetics, n values ($p < 0.001$) for TPH removal were highly significantly correlated with treatment temperature, and k values ($p < 0.05$) were also statistically correlated with temperature. Generally, increasing temperature could enhance TPH removal rate mainly by raising n values. Both k and n values were statistically correlated to S/C mixing ratio ($p < 0.05$) and highly significantly correlated with initial TPH content ($p < 0.001$). k values increased with S/C ratio and thus caused the enhanced TPH removal rates. As the p values of A*C for k and n values and B*C for n values were less than 0.05, there were significant interactions between temperature and initial TPH content affecting k and n values, and between S/C ratio and initial TPH content impacting n values.

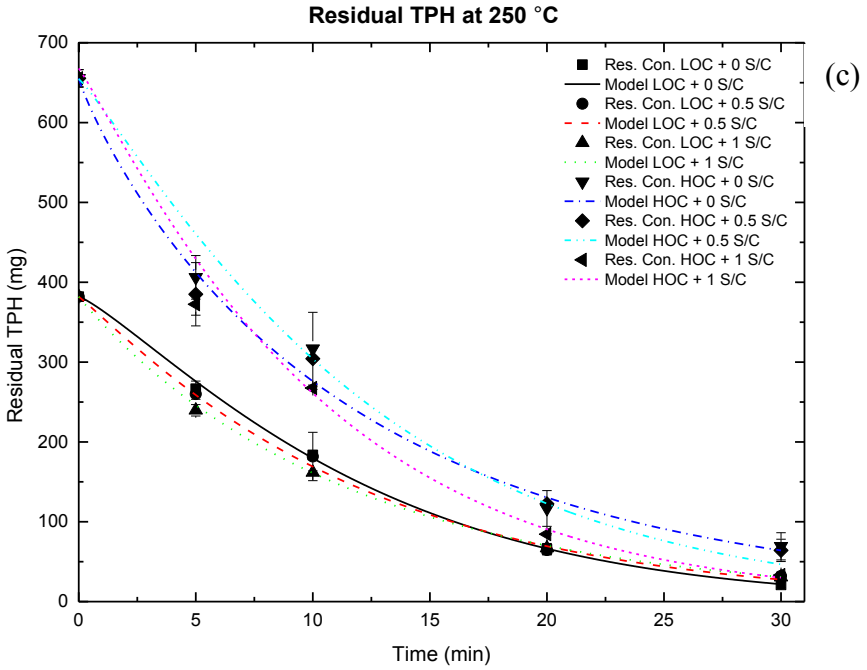
The improvement of TPH removal kinetics curve slopes was observed, and this was more obvious at low temperature and HOCs due to the addition of sand. Similar effects were also observed by Samaksaman et al. (2016a) who studied the removal process of benzene, toluene, ethylbenzene, xylene and PAHs from soil. This indicates that the enhancement of texture and pore size or transport-available porosity of drill cuttings may increase the effective diffusivity of petroleum hydrocarbons in porous media, and the addition of sand may improve the thermal conductivity of soil, thus improving oil removal from OBDCs (Falciglia et al., 2011, Samaksaman et al., 2016a).


Residual TPH at 150 °C
Residual TPH (mg)
Time (min)
Res. Con. LOC + 0 S/C
Model LOC + 0 S/C
Res. Con. LOC + 0.5 S/C
Model LOC + 0.5 S/C
Res. Con. LOC + 1 S/C
Model LOC + 1 S/C
Res. Con. HOC + 0 S/C
Model HOC + 0 S/C
Res. Con. HOC + 0.5 S/C
Model HOC + 0.5 S/C
Res. Con. HOC + 1 S/C
Model HOC + 1 S/C

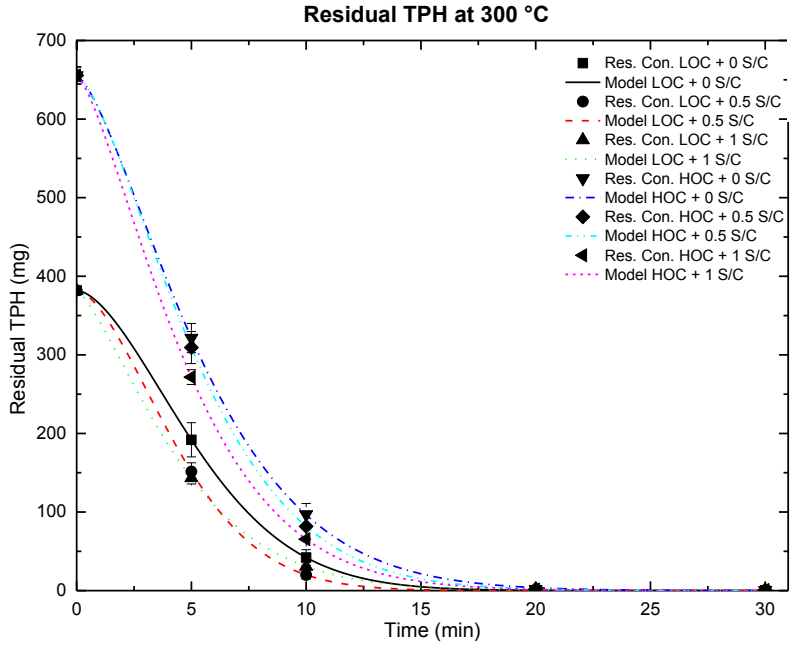
(a)


Residual TPH at 200 °C
Residual TPH (mg)
Time (min)
Res. Con. LOC + 0 S/C
Model LOC + 0 S/C
Res. Con. LOC + 0.5 S/C
Model LOC + 0.5 S/C
Res. Con. LOC + 1 S/C
Model LOC + 1 S/C
Res. Con. HOC + 0 S/C
Model HOC + 0 S/C
Res. Con. HOC + 0.5 S/C
Model HOC + 0.5 S/C
Res. Con. HOC + 1 S/C
Model HOC + 1 S/C

(b)



(c)



(d)

Figure 4.3 Residual TPH by mass and kinetics model curves for LOCs and HOCs at S/C mixing ratio of 0, 0.5 and 1.0 under different treatment temperatures, (a) 150 °C, (b) 200 °C, (c) 250 °C, and (d) 300 °C

Table 4.6 Desorption parameters k (min $^{-1}$) and n and adjusted R^2 of TPH removal kinetics model at temperature of 150, 200, 250 and 300 °C for all the tested OBDCs samples

T(°C)	LOC with S/C of 0				LOC with S/C of 0.5				LOC with S/C of 1.0			
	k	n	Adjusted R^2	Prob>F	k	n	Adjusted R^2	Prob>F	k	n	Adjusted R^2	Prob>F
150	0.0097	1.0419	0.9963	<0.001	0.0565	0.6015	0.9982	<0.001	0.0867	0.4985	0.9999	<0.001
200	0.0305	0.8748	0.9899	<0.001	0.0567	0.7453	0.9994	<0.001	0.1253	0.5139	0.9991	<0.001
250	0.0461	1.2138	0.9998	<0.001	0.0701	1.0657	0.9996	<0.001	0.0918	0.9732	0.9999	<0.001
300	0.0462	1.6790	1.0000	<0.001	0.0627	1.6727	1.0000	<0.001	0.1094	1.3626	1.0000	<0.001
T(°C)	HOC with S/C of 0				HOC with S/C of 0.5				HOC with S/C of 1.0			
	k	n	Adjusted R^2	Prob>F	k	n	Adjusted R^2	Prob>F	k	n	Adjusted R^2	Prob>F
150	0.0973	0.3951	0.9914	<0.001	0.1601	0.3051	0.9881	<0.001	0.1998	0.2360	0.9920	<0.001
200	0.0970	0.5340	0.9952	<0.001	0.1492	0.4807	0.9951	<0.001	0.1883	0.4063	0.9607	<0.05
250	0.1088	0.9002	0.9976	<0.001	0.0575	1.1254	0.9988	<0.001	0.0767	1.0883	0.9899	<0.05
300	0.0715	1.4283	1.0000	<0.001	0.0704	1.4706	1.0000	<0.001	0.0944	1.3876	1.0000	<0.001

Table 4.7 Tests of Between-Subjects Effects for k (min $^{-1}$) and n of TPH desorption kinetics model

Source	Dependent variable	Type III sum of squares	df	Mean square	F	Prob>F
Corrected Model	k	.049 [a]	17	.003	7.848	.009
	n	4.495 [b]	17	.264	68.097	.000
Intercept	k	.195	1	.195	528.101	.000
	n	20.167	1	20.167	5193.614	.000
A: Treatment	k	.005	3	.002	4.760	.050
temperature	n	3.776	3	1.259	324.132	.000
B: Sand/OBDCs	k	.014	2	.007	18.703	.003
mixing ratio (S/C)	n	.164	2	.082	21.053	.002
C: Initial TPH	k	.014	1	.014	37.910	.001
content	n	.257	1	.257	66.275	.000
A * B	k	.006	6	.001	2.559	.139
	n	.083	6	.014	3.562	.074
A * C	k	.010	3	.003	8.962	.012
	n	.103	3	.034	8.874	.013
B * C	k	.001	2	.000	.786	.498
	n	.112	2	.056	14.440	.005
Error	k	.002	6	.000		
	n	.023	6	.004		
Total	k	.246	24			
	n	24.686	24			
Corrected Total	k	.051	23			
	n	4.519	23			

a. R Squared = .957 (Adjusted R Squared = .835)

b. R Squared = .995 (Adjusted R Squared = .980)

* Denotes the interaction between two factors

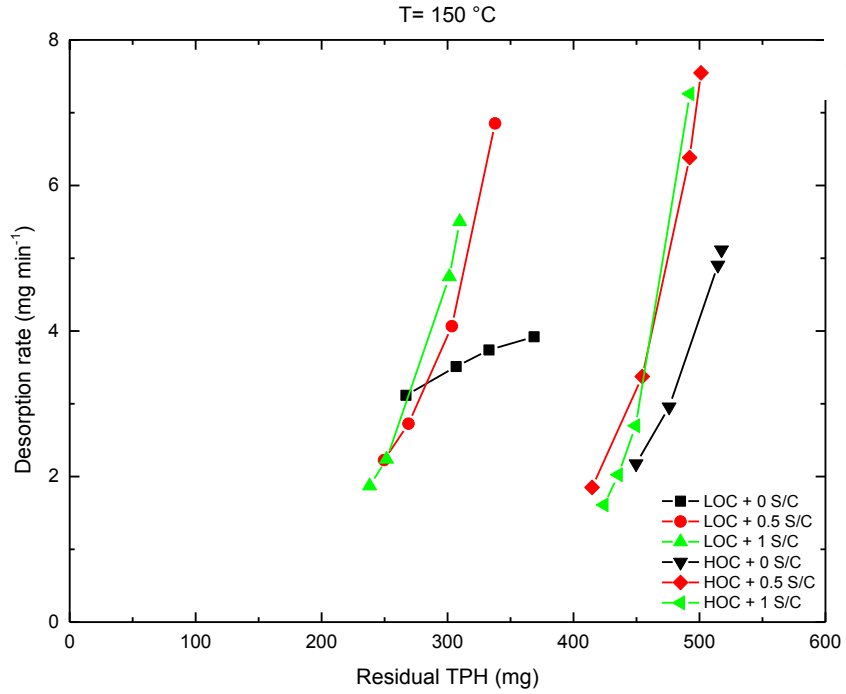
4.5 TPH desorption rate curves

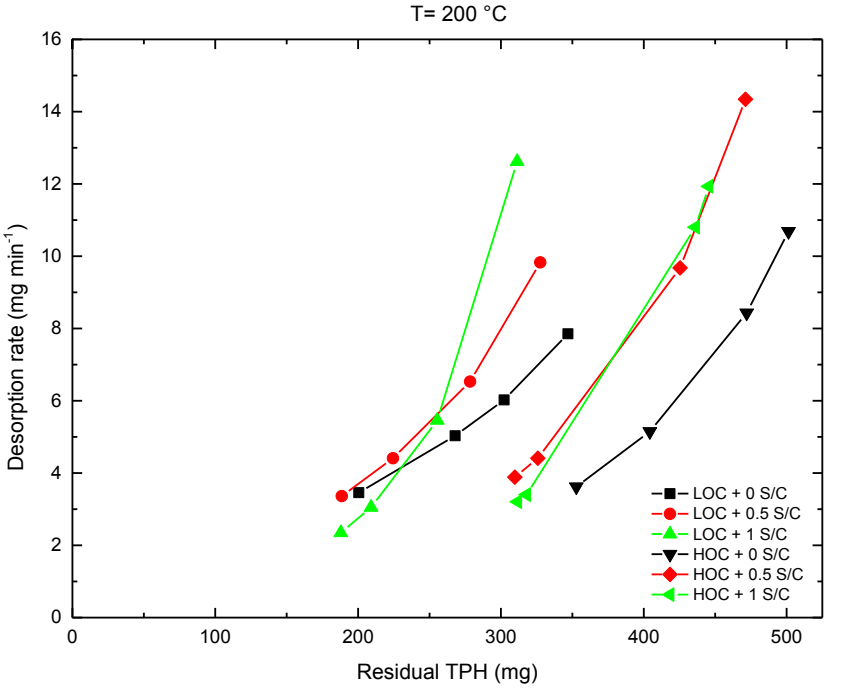
TPH desorption rates in terms of residual TPH contents in all the tested OBDCs samples under the thermal temperatures of 150, 200, 250 and 300 °C were calculated using Eq. (5) and then plotted in Figure 4.4. As expected, TPH desorption rate increased with thermal temperature and the residual TPH content due to the nature of the process (Falciglia et al., 2011). Generally, regardless of initial TPH content, the desorption rates should be similar for similar OBDCs such as (LOC + S/C of 0) and (HOC + S/C of 0) at 250 and 300 °C (Figure 4.4 c and d). However, the desorption rates at lower temperatures (150 and 200 °C, Figure 4.4 a and b) for HOCs were much lower than those desired rates of LOCs at the same residual TPH. This may be due to the limited desorption rate of heavier oil fraction (e.g., F3) at low thermal temperature, and HOCs had much more F3 fractions than LOCs. In addition, thermal conductivity decreases with the increasing soil organic matter such as the oil content in this study (Nidal et al., 2000), which may cause less heat transferring to the HOCs than that to LOCs, thus leading to decreased desorption rate. The difference of desorption rates between LOC and HOC at the same low temperatures (150 and 200 °C) suggested that the kinetics model for temperatures below 250 °C should be examined and fitted when calculating residual TPH concentration or desorption rate or identifying the time required to reach specific target levels of remediation. On the other hand, the kinetics models of TPH desorption developed for temperatures above 250 °C can be used for drill cuttings with different initial TPH content.

The curves of TPH desorption rate could visually display the change of TPH desorption rate with the LTTD treatment under each condition. From the trends of TPH desorption rate curves, it can be suggested that LTTD under 150 and 200 °C do not appear to be an

acceptable remediation technology to reach Canadian recommended management limits for PHCs (Table 3.4). The reason is that desorption rates at 150 and 200 °C may decrease to 0 mg min^{-1} before TPH reduce to 60 mg (i.e., 6000 mg kg^{-1} in 10 g drill cuttings) (Figure 4.4 a and b). However, Figure 4.4 c and d show that TPH desorption rates at 250 and 300 °C did not reduce to 0 mg min^{-1} until PHCs were completely removed. Thus, LTTD under 250 and 300 °C can be eligible for the remediation of OBDCs.

Mostly, desorption rate increased with the addition of sand, especially for OBDCs with high residual TPH. As suggested by Nidal et al. (2000) and Sáez Blázquez et al. (2017), soil thermal conductivity increased with the increasing percentage of sand, which could enhance TPH desorption from OBDCs. However, when residual TPH was less than around 270 mg, the lower desorption rates at 150 °C for LOC + S/C of 0.5 and LOC + S/C of 1.0 than that for LOC + S/C of 0 indicated that the load of sand may inhibit the TPH desorption under low temperature and low residual TPH content conditions. Similar results were also found at 200 °C for LOC + S/C of 0 and LOC + S/C of 1.0. The kinetics curves for 250 and 300 °C suggested that the presence of sand did not have much enhancement but even had some inhibitions of TPH desorption when the residual TPH content was low.


T= 150 °C
(a)
Desorption rate (mg min-1)
Residual TPH (mg)
0
2
4
6
8
0
100
200
300
400
500
600
LOC + 0 S/C
LOC + 0.5 S/C
LOC + 1 S/C
HOC + 0 S/C
HOC + 0.5 S/C
HOC + 1 S/C


T= 200 °C
(b)
Desorption rate (mg min-1)
Residual TPH (mg)
0
2
4
6
8
10
12
14
16
0
100
200
300
400
500
LOC + 0 S/C
LOC + 0.5 S/C
LOC + 1 S/C
HOC + 0 S/C
HOC + 0.5 S/C
HOC + 1 S/C

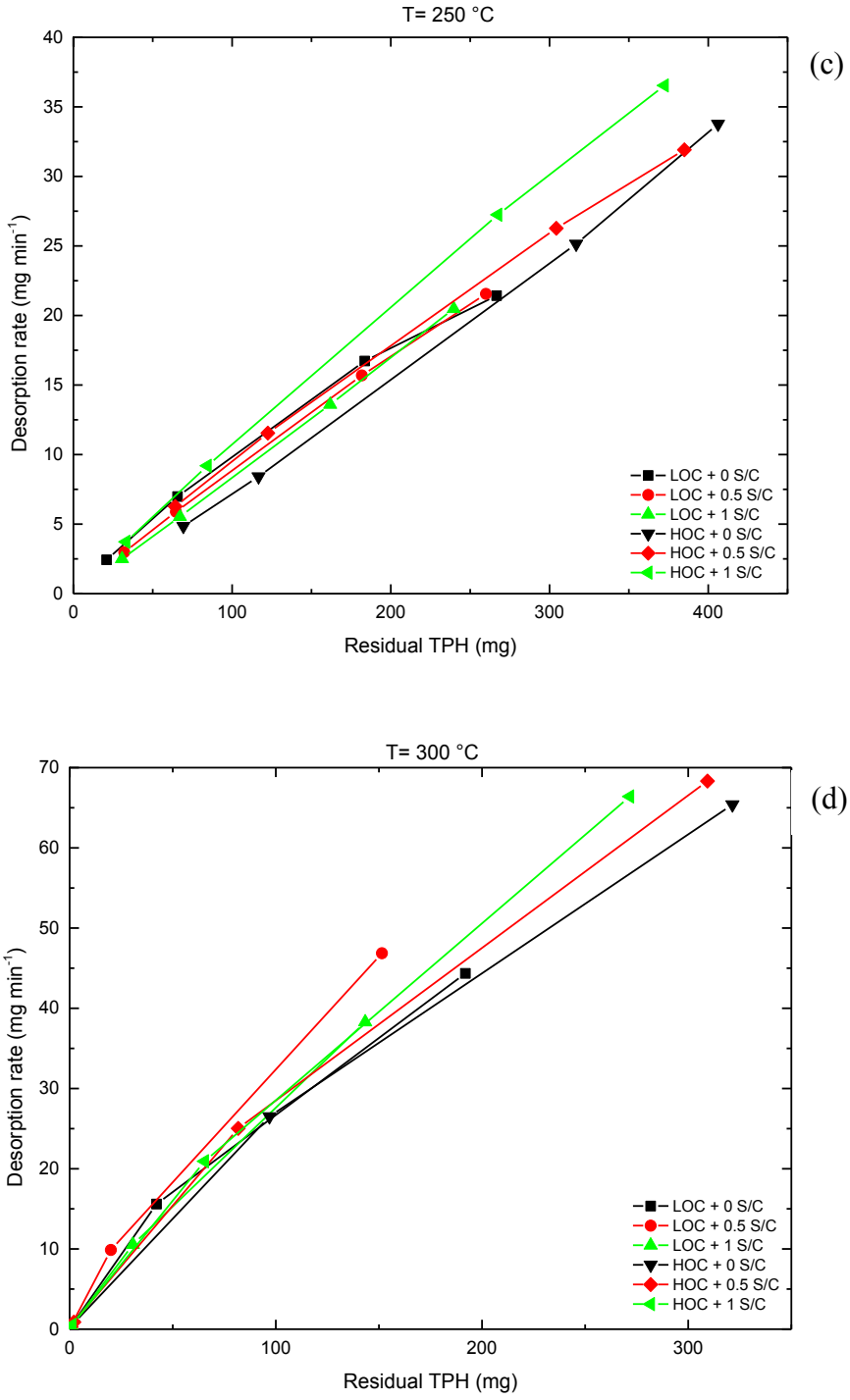


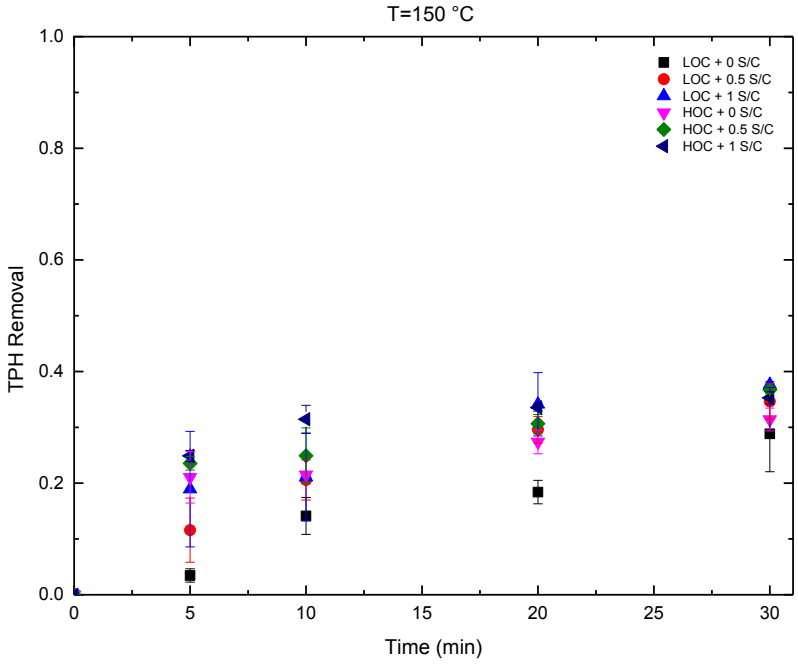
Figure 4.4 Desorption rate as a function of residual TPH mass for LOCs and HOCs at different S/C mixing ratio under different treatment temperatures, (a) 150 °C, (b) 200 °C, (c) 250 °C, and (d) 300 °C

4.6 TPH removal efficiency

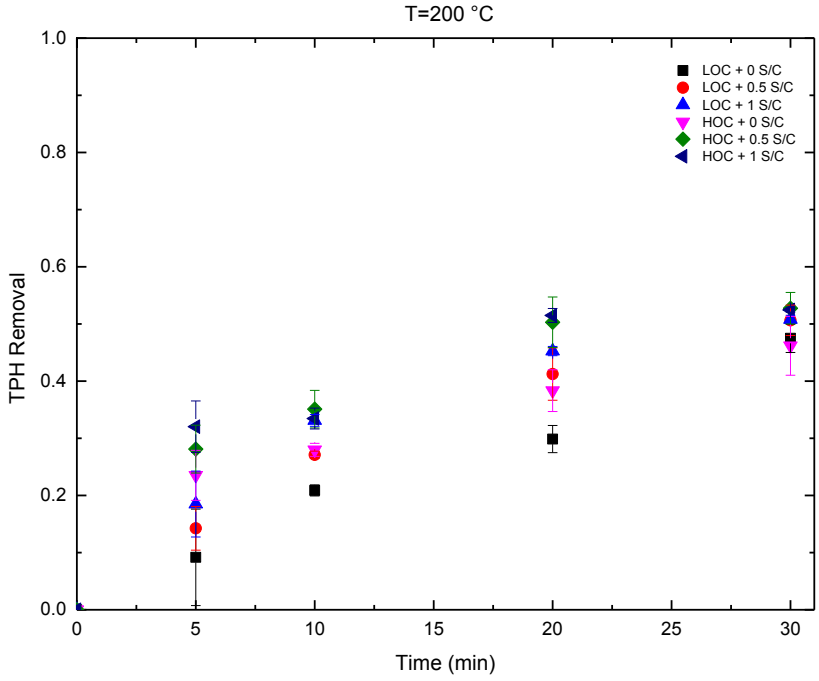
Table 4.8 lists the removal efficiency of TPH in LOCs and HOCs after LTTD treatment at different thermal temperatures, S/C mixing ratios and treatment time. Fig. 4.5 shows the TPH removal efficiency versus treatment time under the four treatment temperatures. At all tested temperatures, the maximum TPH removal efficiency was observed for HOCs with a S/C ratio of 1.0, while the highest TPH removal for LOCs occurred at 300 °C. In addition, the lowest values of TPH removal occurred for LOCs without sand addition. The higher difference (up to 15%) of TPH removal efficiency among OBDCs added with different mixing ratio of sand during LTTD treatment was found at the lower treatment temperatures (150 and 200 °C). High TPH removal efficiency (94.76% at LOC + S/C of 0.5) was observed at 300 °C in a short treatment duration (10 min), whereas 250 °C of treatment temperature required a longer time (30 min) to achieve 94.93% of TPH removal for HOC with S/C ratio of 1.0.

Table 4.9 shows the tests of between-subjects effects for TPH removal efficiency. Fig. 4.6 and 4.7 present the main effect plot and the interaction plots for the removal efficiency. As shown in Fig. 4.6, the TPH removal was improved with the increase of values of all four tested factors. The influential effects were ranked as treatment temperature (A) > treatment time (D) > S/C ratio (B) > initial TPH content (C), as indicated by the values of type III sum of squares in Table 4.9. The highest TPH removal (99.92%) occurred in HOC with S/C ratio of 1.0 after 30 min of treatment under the temperature of 300 °C. With respect to the interaction effects on TPH removal (Fig. 4.7), it can be found that significant interaction occurred between treatment temperature and S/C ratio, treatment temperature and initial TPH content, treatment temperature and time, as well as between initial TPH content and

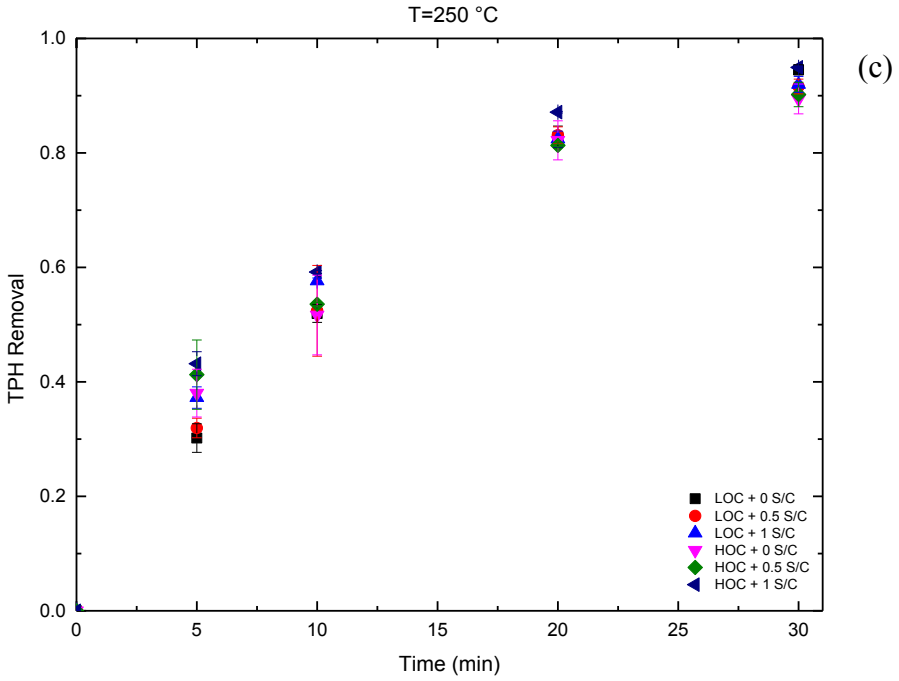
treatment time. The tests of between-subjects effects (Table 4.9) also revealed such interactions since p values for A*B, A*C and C*D were less than 0.05 (significant), while p value for A*D was less than 0.001 (highly significant).


T=150 °C
TPH Removal
Time (min)
LOC + 0 S/C
LOC + 0.5 S/C
LOC + 1 S/C
HOC + 0 S/C
HOC + 0.5 S/C
HOC + 1 S/C
0.0
0.2
0.4
0.6
0.8
1.0
0
5
10
15
20
25
30

(a)


T=200 °C
TPH Removal
Time (min)
LOC + 0 S/C
LOC + 0.5 S/C
LOC + 1 S/C
HOC + 0 S/C
HOC + 0.5 S/C
HOC + 1 S/C
0.0
0.2
0.4
0.6
0.8
1.0
0
5
10
15
20
25
30

(b)



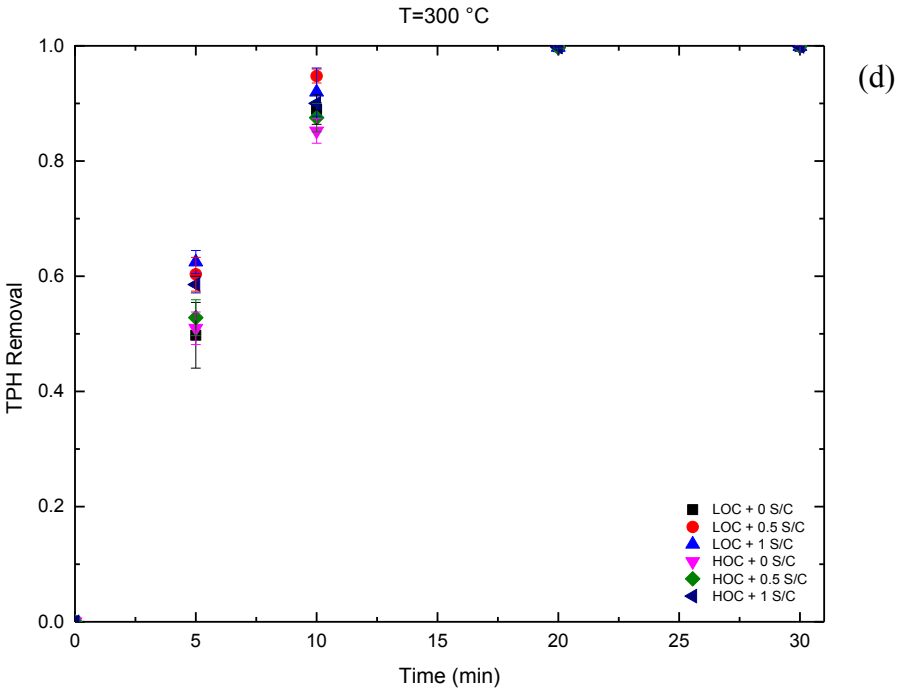


Figure 4.5 TPH removal efficiency as a function of treatment time under different treatment temperatures, (a) 150 °C, (b) 200 °C, (c) 250 °C, and (d) 300 °C

Table 4.8 TPH removal efficiency (R_e) under different LTTD treatment conditions

Coded factors				R_e (%)	SD	Coded factors				R_e (%)	SD	Coded factors				R_e (%)	SD	Coded factors				R_e (%)	SD
A	B	C	D			A	B	C	D			A	B	C	D			A	B	C	D		
1	1	1	1	3.46	0.0119	3	1	1	1	30.18	0.0250	1	1	2	1	21.05	0.0461	3	1	2	1	38.03	0.0417
1	1	1	2	12.85	0.0149	3	1	1	2	51.94	0.0154	1	1	2	2	21.50	0.0008	3	1	2	2	51.67	0.0695
1	1	1	3	19.67	0.0031	3	1	1	3	82.81	0.0188	1	1	2	3	27.39	0.0214	3	1	2	3	82.20	0.0341
1	1	1	4	30.10	0.0502	3	1	1	4	94.52	0.0089	1	1	2	4	31.40	0.0204	3	1	2	4	89.43	0.0260
1	2	1	1	11.58	0.0575	3	2	1	1	31.94	0.0171	1	2	2	1	23.54	0.0120	3	2	2	1	41.27	0.0605
1	2	1	2	20.56	0.0359	3	2	1	2	52.41	0.0793	1	2	2	2	24.92	0.0499	3	2	2	2	53.58	0.0026
1	2	1	3	29.58	0.0238	3	2	1	3	83.09	0.0147	1	2	2	3	30.66	0.0164	3	2	2	3	81.31	0.0022
1	2	1	4	34.65	0.0317	3	2	1	4	91.61	0.0129	1	2	2	4	36.73	0.0072	3	2	2	4	90.21	0.0213
1	3	1	1	18.93	0.1035	3	3	1	1	37.26	0.0188	1	3	2	1	24.88	0.0099	3	3	2	1	43.18	0.0210
1	3	1	2	21.08	0.0785	3	3	1	2	57.63	0.0052	1	3	2	2	31.45	0.0249	3	3	2	2	59.19	0.0026
1	3	1	3	34.13	0.0568	3	3	1	3	82.43	0.0139	1	3	2	3	33.55	0.0065	3	3	2	3	87.11	0.0014
1	3	1	4	37.65	0.0051	3	3	1	4	91.98	0.0139	1	3	2	4	35.28	0.0108	3	3	2	4	94.93	0.0009
2	1	1	1	9.17	0.0844	4	1	1	1	49.75	0.0570	2	1	2	1	23.51	0.0438	4	1	2	1	50.96	0.0283
2	1	1	2	20.88	0.0097	4	1	1	2	88.96	0.0258	2	1	2	2	27.98	0.0114	4	1	2	2	85.22	0.0213
2	1	1	3	29.86	0.0238	4	1	1	3	99.85	0.0004	2	1	2	3	38.33	0.0366	4	1	2	3	99.75	0.0003
2	1	1	4	47.50	0.0249	4	1	1	4	99.92	0.0000	2	1	2	4	46.18	0.0515	4	1	2	4	99.94	0.0000
2	2	1	1	14.25	0.0383	4	2	1	1	60.34	0.0293	2	2	2	1	28.11	0.0418	4	2	2	1	52.81	0.0311
2	2	1	2	27.11	0.0063	4	2	1	2	94.76	0.0120	2	2	2	2	35.09	0.0328	4	2	2	2	87.52	0.0246
2	2	1	3	41.24	0.0458	4	2	1	3	99.87	0.0002	2	2	2	3	50.29	0.0442	4	2	2	3	99.69	0.0005
2	2	1	4	50.63	0.0266	4	2	1	4	99.93	0.0001	2	2	2	4	52.75	0.0276	4	2	2	4	99.90	0.0001
2	3	1	1	18.50	0.0577	4	3	1	1	62.47	0.0200	2	3	2	1	32.03	0.0451	4	3	2	1	58.55	0.0144
2	3	1	2	33.13	0.0104	4	3	1	2	91.96	0.0418	2	3	2	2	33.46	0.0182	4	3	2	2	90.01	0.0015
2	3	1	3	45.26	0.0081	4	3	1	3	99.74	0.0009	2	3	2	3	51.49	0.0122	4	3	2	3	99.81	0.0005
2	3	1	4	50.80	0.0073	4	3	1	4	99.89	0.0001	2	3	2	4	52.45	0.0039	4	3	2	4	99.90	0.0003

SD: standard deviation

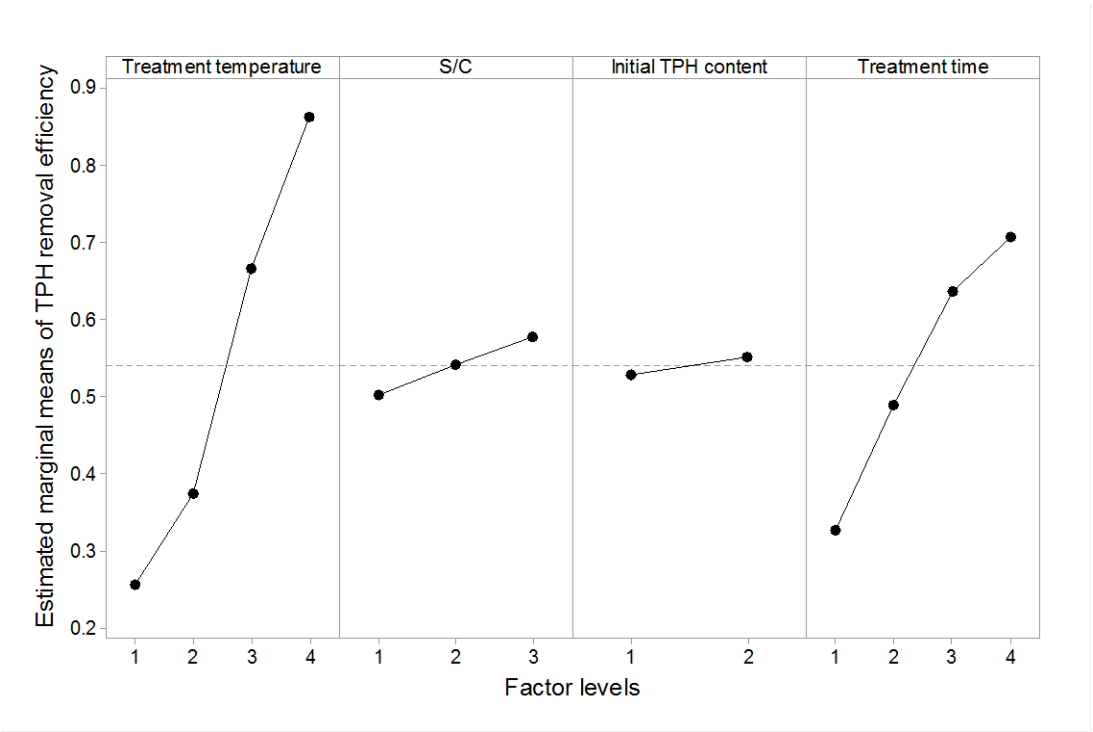


Figure 4.6 Main effect plot of experimental factors on the TPH removal efficiency

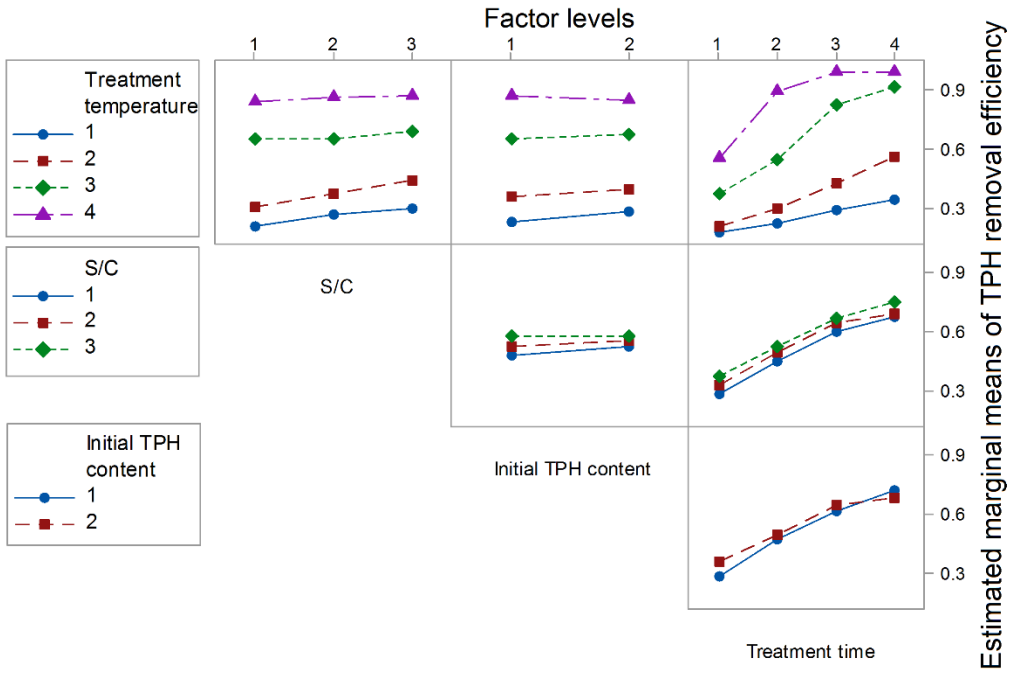


Figure 4.7 Interaction of experimental factors on TPH removal efficiency

Table 4.9 Tests of between-subjects effects for TPH removal efficiency

Source	Type III sum of squares	df	Mean square	F	Prob>F
Corrected Model	8.162[a]	38	.215	97.138	.000
Intercept	28.009	1	28.009	12667.519	.000
A: Treatment temperature, °C	5.476	3	1.825	825.536	.000
B: Sand/OBDCs mixing ratio (S/C)	.091	2	.046	20.627	.000
C: Initial TPH content	.014	1	.014	6.227	.015
D: Treatment time	2.038	3	.679	307.239	.000
A * B	.030	6	.005	2.276	.049
A * C	.019	3	.006	2.878	.044
A * D	.451	9	.050	22.652	.000
B * C	.005	2	.003	1.158	.321
B * D	.003	6	.001	.257	.954
C * D	.034	3	.011	5.138	.003
Error	.126	57	.002		
Total	36.296	96			
Corrected Total	8.288	95			

a. R Squared = .985 (Adjusted R Squared = .975)

* Denotes the interaction between two factors

4.7 Energy consumption and cost optimization

High oil removal efficiencies are hardly achievable for drill cuttings contaminated with high content of hydrocarbons when using other economical treatments such as natural biodegradation (Steliga and Jakubowicz, 2010) or even using more expensive treatments such as supercritical fluid extraction (Goodarznia and Esmaeilzadeh, 2006). Microwaves treatment could quickly and effectively reduce TPH content in OBDCs, but it requires a higher energy consumption and consequently a higher cost (Robinson et al., 2009; Falciglia et al., 2011). In this study, high TPH removal efficiencies were observed when using LTTD treatment for OBDCs. The energy consumptions (kWh) for LTTD at four treatment temperatures were recorded and plotted in terms of treatment time (Fig. 4.8). The treatment time was started after the LTTD system reached target temperature. The intercept in the figure represents the consumed energy for the LTTD system heating up to each target temperature from room temperature (25 °C). As shown in the figure, energy consumption for the LTTD treatment was linearly related to the treatment time ($R^2 > 0.99$) and increased with temperature. Thus, energy consumption at a specific treatment temperature and treatment time could be calculated with fitted equations shown in Fig. 4.8.

To achieve Canadian management limits shown in Table 3.5 (i.e. F2 $\leq$ 1000 mg kg $^{-1}$ and F3 $\leq$ 5000 mg kg $^{-1}$), the remediation time for LTTD treatment of LOCs and HOCs with different S/C ratios under different treatment temperatures was assessed by using the desorption kinetics and the initial contents of F2 and F3 (Table 4.10). It was found that the LTTD treatment to reach F3 management limit took much longer time than F2. As a result, only remedial time for F3 was considered for cost optimization. It was evident that the remediation at 150 and 200 °C took too long, and thus only costs at 250 and 300 °C were

determined and shown in Table 4.11. From the table, the best treatment conditions for LOC to both reach Canadian management limits and minimum costs were found as 5.7 min of LTTD treatment at 300 °C with S/C ratio of 1.0, which costs about $CAD 72 – 92 per ton of drill cuttings, as compared to the cost of about $CAD176 and 98 per ton at 250 and 300 °C without sand addition, respectively. Similarly, it costs about $CAD100 – 121 per ton of HOC drill cuttings with S/C ratio of 1.0 at 300 °C for 8.5 min LTTD treatment, as compared to $CAD304 and 133 per ton for treatments without sand addition at 250 and 300 °C, respectively. Therefore, the assessment of optimal conditions of LTTD with minimum costs while reaching specific standard limits is more meaningful.

According to US Technical Report (NFESC, 1998), typical treatment cost is $USD 25 – 200 per ton for continuous-feed thermal desorption technologies and $USD 28 – 250 per ton for batch-feed thermal desorption technologies, which are comparable to ex-situ bioremediation cost ($USD 24 – 380 per ton) reported by US EPA (SWER, 2004). Moreover, based on the findings in this study, treatment period, energy consumption and environmental impacts could be minimized. Consequently, LTTD process appears to be a better choice for the remediation of OBDCs especially due to their high efficiency and cost effectiveness.

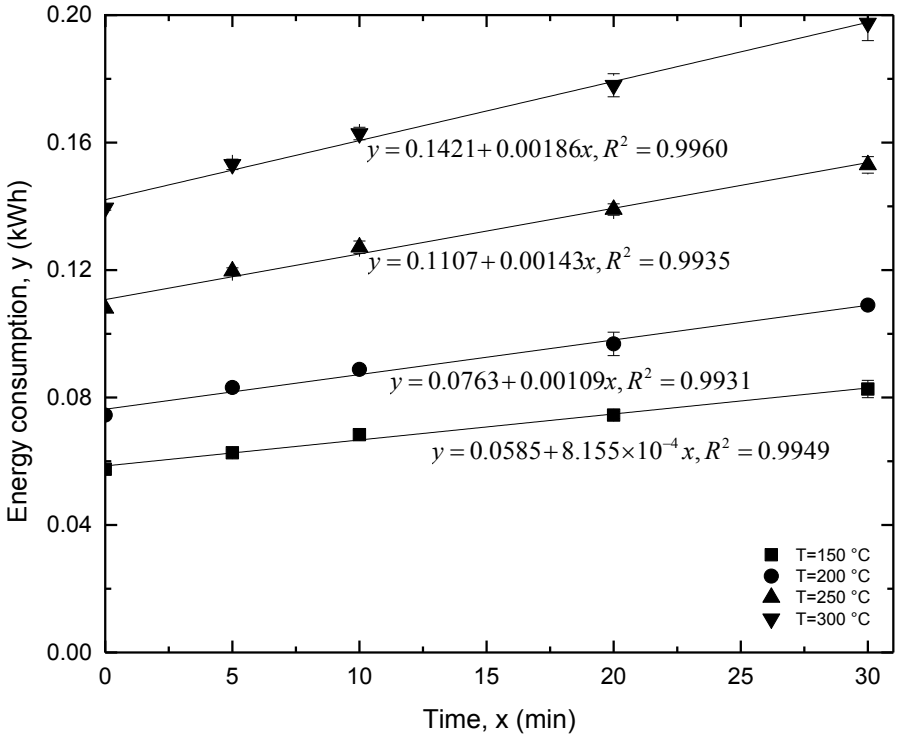


Figure 4.8 Energy consumption of the LTTD system

Table 4.10 Assessed remedial time for LTTD treatment to achieve Canadian management limits

	LOC + S/C of 0		LOC + S/C of 0.5		LOC + S/C of 1.0		HOC + S/C of 0		HOC + S/C of 0.5		HOC + S/C of 1.0	
T(°C)	Initial F2 (mg kg $^{-1}$)	Time (min)	Initial F2 (mg kg $^{-1}$)	Time (min)	Initial F2 (mg kg $^{-1}$)	Time (min)	Initial F2 (mg kg $^{-1}$)	Time (min)	Initial F2 (mg kg $^{-1}$)	Time (min)	Initial F2 (mg kg $^{-1}$)	Time (min)
150		120		87		94		372		1542		1255
200	15370	35.4	10247	35.3	7685	26.3	20931	71.8	13954	44	10465	28.2
250		16.7		15.3		13.5		23.9		18.8		17.6
300		7.1		6.3		5.6		7.6		7.2		6.5
	LOC + S/C of 0		LOC + S/C of 0.5		LOC + S/C of 1.0		HOC + S/C of 0		HOC + S/C of 0.5		HOC + S/C of 1.0	
T(°C)	Initial F3 (mg kg $^{-1}$)	Time (min)	Initial F3 (mg kg $^{-1}$)	Time (min)	Initial F3 (mg kg $^{-1}$)	Time (min)	Initial F3 (mg kg $^{-1}$)	Time (min)	Initial F3 (mg kg $^{-1}$)	Time (min)	Initial F3 (mg kg $^{-1}$)	Time (min)
150		344		3294		1573		2550811		15727		30116
200	22824	273	15216	199	11412	1367	44617	175390	29745	1882	22308	2608
250		22		17.5		13.1		38.1		27.4		17.8
300		9.4		6.5		5.7		12.8		10.3		8.5

Table 4.11 Estimated cost ($CAD per ton of OBDCs) of LTTD based on energy consumption curves and remedial time of F3 [a]

T(°C)	LOC + S/C of 0	LOC + S/C of 0.5			LOC + S/C of 1.0			HOC + S/C of 0	HOC + S/C of 0.5			HOC + S/C of 1.0		
	Thermal cost [b]	Thermal cost	Sand cost [c]	Total cost [d]	Thermal cost	Sand cost	Total cost	Thermal cost	Thermal cost	Sand cost	Total cost	Thermal cost	Sand cost	Total cost
150	ND	ND		ND	ND		ND	ND	ND		ND	ND		ND
200	ND	ND		ND	ND		ND	ND	ND		ND	ND		ND
250	176	139	6 - 16.5	145 - 155.5	104	12 - 33	116 - 137	304	219	6 - 16.5	225 - 235.5	142	12 - 33	154 - 175
300	98	68		74 - 84.5	59		71 - 92	133	107		113 - 123.5	88		100 - 121

a. 20 g of OBDCs can be treated in the LTTD system by using two quartz tube each time

b. Thermal cost = slope of energy cost curve at each temperature × remedial time per ton×0.1116 (0.1116 $CAD per kWh is energy charge for small general business service from BC hydro)

c. Sand cost is 12 – 33 per ton depending on the usages from www.sharecost.ca

d. Total cost = thermal cost + sand cost

ND: not determined

Chapter 5 Conclusions

5.1 Research summary

This study used a bench-scale apparatus to investigate the remediation of OBDCs by LTTD process. The following conclusions have been obtained.

The physicochemical properties of base soil for artificial drill cuttings before and after LTTD (at 300 °C 20 min) were analyzed. It was found that the sand, EC, TC, and the available PO_4-P contents in HOC after LTTD were increased and the pH was closer to neutral compared to those in base soil. Although the organic matter was significantly decreased, the overall soil health was improved since the PHCs was barely left in the HOC after LTTD treatment, which could significantly reduce the bio-toxicity of drill cuttings. Compared to completely removal of PHCs from OBDCs, optimal treatment conditions for LTTD will be more beneficial and can maximally keep soil health. Therefore, LTTD could be a better alternative to other remediation methods (e.g., Fenton reaction and soil washing treatment) that deteriorated soil fertility and ecological soil functions (Laurent et al., 2012; Yi and Sung, 2015).

The kinetics models for F2, F3 and TPH desorption from OBDCs under different LTTD treatment conditions were established and compared:

(1) The nonlinear least-squares exponential kinetics model exhibited a great correlation (adjusted $R^2 > 0.9$) with the experimental data for residual F2, F3 and TPH content in all the treated OBDCs samples. The desorption rates of F3 under each treatment temperature were much lower than those of F2. The slopes of TPH removal kinetics curves were less than

those of F2 but greater than those of F3, although the TPH desorption kinetics were more similar to that of F3 fraction.

(2) Generally, increasing treatment temperature could enhance F2, F3 and TPH removal rate mainly by raising n values, while the addition of sand mainly assisted hydrocarbons desorption by improving k values. Initial TPH content also significantly affected k and n values for F3 and TPH desorption but not for F2 removal.

(3) The increase of slopes for TPH removal kinetics curves was observed and was more obvious at low temperature and HOCs due to the addition of sand, which may be caused by increased effective diffusivity of hydrocarbons in porous media.

The curves of desorption rates vs residual TPH mass were plotted to assess the influences of treatment temperature, sand/OBDCs mixing ratio, and initial TPH content on the contaminant desorption:

(1) TPH desorption rate increased with treatment temperature and residual TPH content due to the nature of LTTD process. Regardless of the initial TPH content, the desorption rates were similar at similar residual TPH contents for LOC and HOC without sand addition at 250 and 300 °C. The difference of desorption rates between LOC and HOC at the same low temperatures (150 and 200 °C) suggested that the kinetics models for temperatures below 250 °C should be specifically fitted when calculating desorption rate or identifying the time required to reach specific target levels of remediation. On the other hand, the kinetics models of TPH desorption for temperature above 250 °C may be applied to other drill cuttings with similar characteristics.

(2) Mostly, desorption rate increased with the addition of sand, especially for OBDCs with high residual TPH, which may be resulted from increased thermal conductivity by the increasing percentage of sand. However, the load of sand may inhibit the TPH desorption at conditions of low temperature and low TPH content.

The effects of treatment temperature, time, sand/OBDCs mixing ratio, and initial TPH content on LTTD treatment were evaluated:

(1) High TPH removal efficiency (94.76% for LOC + S/C of 0.5) could be reached at 300 °C in a short period (10 min), whereas 250 °C of LTTD treatment required a longer time (30 min) to achieve 94.93% of TPH removal for HOC with S/C ratio of 1.0.

(2) The TPH removal improved with the increase of all four tested factors, and the influential effects were ranked as treatment temperature (A) > treatment time (D) > S/C ratio (B) > initial TPH content (C). The highest TPH removal (99.92%) was observed in HOC with S/C ratio of 1.0 treated at 300 °C for 30 min.

The optimal treatment conditions of achieving specific remediation levels with minimum cost were estimated by using model parameters and recorded energy consumption:

(1) Energy consumption for the thermal reactor was linearly related to the treatment time ($R^2 > 0.99$) and increased with temperature.

(2) The best treatment conditions to both reach Canadian management limits (i.e. F2 ≤ 1000 mg kg^{-1} and F3 ≤ 5000 mg kg^{-1}) and minimum costs, were 5.7 min of LTTD treatment at 300 °C for LOC with S/C ratio of 1.0, costing about $CAD 71 – 92 per ton of drill cuttings. It may cost about $CAD 100 – 121 per ton of drill cuttings for HOC with S/C ratio

of 1.0 at 300 °C after 8.5 min of treatment, as compared to $CAD 304 and 133 per ton for treatments without sand addition at 250 and 300 °C, respectively.

(3) LTTD process appears to be a great choice for the remediation of OBDCs especially due to its high efficiency and cost effectiveness.

5.2 Limitations and future research

In this study, the beach-scale LTTD treatment was investigated to remove PHCs from OBDCs with high efficiency and low cost. Considering its cost-effectiveness and applicability to large scale, the LTTD treatment is of great advantages over others. However, little amount of oil was recovered (not shown in the thesis) by the hexane traps, as most of the oil condensed and aggregated at the end of the tube wall due to the low thermal temperature and poor heat-insulation system. The oil recovery should be improved and its reusability should be evaluated if considering the economic value of oil recovery. As for application, rotary dryer/screw could be used as industrial-scale thermal reactor to reduce the cost for mixing sand and drill cuttings. Cheap sand or sandy soil should be tested and used to reduce sand addition cost.

Only the physiochemical properties of one type of drill cuttings without sand addition before and after LTTD treatment were tested in the study. In the future, the effects of temperature, treatment time and sand addition on the properties (including physical, chemical and ecological characteristics) changes will be helpful to better evaluate the reusability of treated drill cuttings for agriculture or other purposes. The impacts of the properties (e.g., structure, diameter, or pore size) of sand on the oil removal efficiency should also be examined to help choose the best mixing sand. To reduce treatment cost, the future study of

beneficial reuse methods for drill cuttings after LTTD treatment such as road spreading, fill material at landfills or as aggregates in concrete or bricks, or restoring coastal wetlands are valuable.

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